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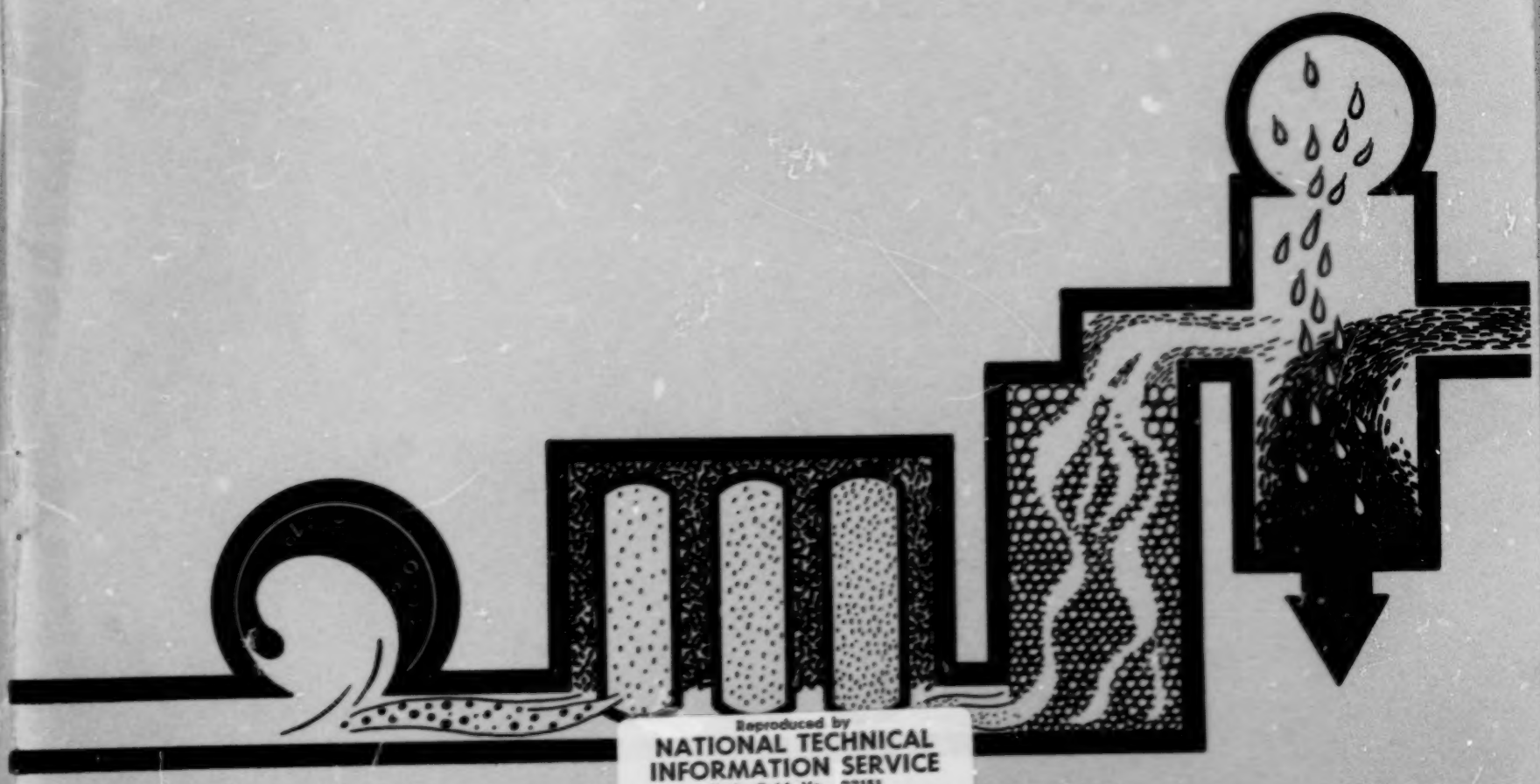
NEW AND ULTRATHIN MEMBRANES FOR MUNICIPAL WASTEWATER TREATMENT BY REVERSE OSMOSIS



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27 Abstract

44 various polysaccharide mixed esters and ethers were tested on microporous supporting films for improved reverse osmosis treatment of municipal waste waters. Cellulose methyl sulfonate O-Propyl sulfonic acid (CMSOPSA) and cellulose acetate O-Propyl sulfonic acid (CAOPSA), at thicknesses between 250 and 5000 angstroms, exhibited water flux in excess of 40 gfd. The CMSOPSA membrane, at 370 angstroms thickness, rejected 96% TDS, 93% nitrates, 96% ammonia, 89% total dissolved organic carbon, and 99% phosphate. Long term (150 hours) testing of the CMSOPSA membrane resulted in an average water flux of 34 to 36 gfd over the last 100 hours, with 93% rejection for TDS, 94% for ammonia, and 83% for total organic carbon. A common enzyme presoak was efficient in restoring fouled membranes to a like-new condition. Similar rejections have been obtained with commercially available membranes, but at fluxes of less than 15 gfd. Preliminary hydrolysis degradation studies established the polymer membrane as superior to the cellulose acetate membrane in resisting degradation. Preliminary optimization studies also established that by: (1) rigorously controlling polymer preparation; (2) optimizing the casting procedures; (3) using a polysulfone support film; (4) optimizing the annealing conditions; and (5) making the membrane as thin as possible, it should be possible to produce a CMSOPSA membrane better than any presently available commercial membrane at about 40¢/ft^2. (Lowry-Texas)

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NEW AND ULTRATHIN MEMBRANES FOR MUNICIPAL WASTEWATER TREATMENT BY REVERSE OSMOSIS

by

North Star Research and Development Institute
Minneapolis, Minnesota 55406

for the

WATER QUALITY OFFICE

ENVIRONMENTAL PROTECTION AGENCY

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ABSTRACT

A series of new and ultrathin membranes with thicknesses from 250 to 5000 angstroms (1×10^{-6} to 2×10^{-5} inch) and consisting of various polysaccharide mixed esters and ethers were tested on microporous supporting films for improved reverse osmosis treatment of municipal wastewaters. From the screening studies with secondary effluent, ultrathin membranes prepared from two polymers (out of a total of 44) looked very promising: cellulose methyl sulfonate O-propyl sulfonic acid (CMSOPSA) and cellulose acetate O-propyl sulfonic acid (CAOPSA). The CAOPSA membrane at a thickness of 370 angstroms exhibited a water flux of 43 gallons per square foot per day (gfd) and rejections of 96 percent for total dissolved solids, 93 percent for nitrates, 96 percent for ammonia, 89 percent for total dissolved organic carbon, and 99 percent for phosphate. The CMSOPSA membrane was found to be significantly less degradable by hydrolysis, and thus more stable than cellulose acetate.

Long-term (150 hours) testing of the CMSOPSA membrane with secondary effluent resulted in an average water flux of 34 to 36 gfd over the last 100 hours, and rejections of 96 percent for total dissolved solids, 94 percent for ammonia, and 83 percent for total organic carbon. The long-term flux decline (not due to fouling) was virtually zero over the last 100 hours of the test. A treatment with an enzyme-active laundry presoaking product was found to be effective in cleaning the membranes and restoring the flux to levels existing before fouling.

Preliminary membrane optimization studies showed that the reverse osmosis properties of these new membranes could be improved by closely controlling the polymer preparation procedures and the casting and annealing conditions. The ultrathin nature of the membranes was an important factor in imparting high flux properties to these membranes.

A preliminary economic analysis showed that, for a tubular configuration, a cost of approximately ten cents could be expected for one square foot of the composite of membrane and microporous support film. This cost was insensitive to polymer raw material costs.

This report was submitted in fulfillment of Project Number 17020EFA, Contract 14-12-587, under the sponsorship of the Water Quality Office, Environmental Protection Agency.

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CONCLUSIONS

This program has resulted in a number of important conclusions on the feasibility and ultimate use of new polymeric ultrathin membranes for treatment of municipal wastewater by reverse osmosis. These conclusions are listed below.

1. Ultrathin membranes of unusual new polymers are technically feasible for treatment of municipal wastewaters by reverse osmosis. New types of membrane materials have demonstrated high potential for an optimum combination of water flux and rejection at a low cost.

2. Ultrathin membranes of two new polymer materials were the most promising of the 44 tested on secondary effluent during the screening studies. These were cellulose methyl sulfonate O-propyl sulfonic acid (CMSOPSA) and cellulose acetate O-propyl sulfonic acid (CAOPSA). Both membranes, at thicknesses around 500 Å, exhibited water fluxes above 40 gallons per square foot per day (gfd) with the following rejections: phosphate, above 99 percent; total dissolved solids, above 95 percent; and ammonia, above 93 percent. For CMSOPSA and CAOPSA, the dissolved organic rejection was 93 and 89 percent, respectively, and the nitrate rejection was 81 and 93 percent, respectively.

3. The performance of an ultrathin CMSOPSA membrane during a 150-hour, long-term test with a secondary effluent feed was outstanding. During this test, in which the membrane was cleaned with Biz* (a common household laundry presoaking product) every twenty hours, the membrane exhibited an average flux of 35 gfd (varying from 55 to 30 between cleanings) and the following rejections: total dissolved solids – 96 percent; ammonia – 94 percent; and dissolved organics – 83 percent. The average flux between cleaning did not decline after the first forty hours.

4. Commercially available asymmetric cellulose acetate membranes exhibited significantly lower water fluxes (less than 15 gfd for 150 hours) than the ultrathin CMSOPSA membranes, although the rejections were similar.

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5. Preliminary hydrolysis degradation studies (by pH effect) showed that ultrathin CMSOPSA membranes were significantly more resistant to basic hydrolysis than were the ultrathin cellulose acetate membranes. Thus, in actual use, CMSOPSA membranes may require fewer replacements than cellulose acetate membranes.

6. Ultrathin cellulose acetate membranes exhibited water fluxes and rejections similar to those of ultrathin CMSOPSA and CAOPSA membranes. However, ultrathin membranes of these new polymers have greater potential for more efficient and low cost applications than do ultrathin cellulose membranes because of (1) their greater resistance to hydrolysis, and (2) the expected improvement in reverse osmosis properties of CMSOPSA and CAOPSA with structural and process optimization.

7. Preliminary optimization studies of the new membranes identified the variables that must be controlled to improve the reverse osmosis performance. By (1) rigorously controlling the polymer preparation; (2) optimizing the casting procedures; (3) using a polysulfone support film; (4) optimizing the annealing conditions; and (5) producing as thin a membrane as practical, it should be possible to produce a CMSOPSA membrane that has significantly better reverse osmosis performance than any membrane commercially available today.

8. A preliminary cost analysis showed that CMSOPSA or other unusual polymer materials combined with a polysulfone support film in a tube would cost about 10 cents per square foot, exclusive of the tube.

RECOMMENDATIONS

This program has consisted primarily of screening new and ultrathin membranes for reverse osmosis treatment of municipal wastewater. The scope of this program did not include rigorous optimization, engineering considerations, or field demonstrations. Because some important new candidate membranes have resulted from this program, it is recommended that it be continued in order to realize fully the practical advantages of these membranes.

The first step that should be carried out in a second phase of this program is optimization of the reverse osmosis properties of ultrathin membranes of cellulose methyl sulfonate O-propyl sulfonic acid (CMSOPSA) and cellulose acetate O-propyl sulfonic acid (CAOPSA). The following properties must be adjusted for optimum performance:

- The polymer synthesis procedures must be investigated and controlled to produce polymers of known purity and predictable degrees of substitution. Thus, the exact polymer structure that would give optimum performance would be elucidated.

- Casting procedures in the most applicable configuration (probably tubes) must be optimized. Optimization would include investigation of polymer casting-solution concentrations, casting solvents, additives (such as surfactants) to the water or casting solution, and environmental conditions.

- The effect of annealing on water flux and rejections must be determined.

- The production of as thin a membrane as practicable in a consistent manner must be investigated.

The optimization testing would include long-term reverse osmosis tests with secondary effluent (up to 500 hours) during which membrane cleaning and feed pretreatment procedures would be investigated and optimized.

A second step in this proposed program would include engineering studies and should yield a more comprehensive estimate of costs and serve as a basis for preparation of a field demonstration of these new membranes. These considerations would lead directly to a third phase which would consist of a demonstration at a sewage treatment plant.

It is also recommended that a small effort, concurrent with the above, be carried out to develop some of the more promising high-flux membranes, such as the cellulose acetate adduct of methylol phenol, that could not be explored in depth during this current program.

INTRODUCTION

Treatment of municipal wastewaters by reverse osmosis has great potential as a simple, effective, and inexpensive method to obtain nearly complete removal of both dissolved and particulate contaminants. To realize this potential fully, new membranes with high water fluxes and high rejections of the various contaminants are necessary. In the program described here, a series of new and ultrathin membranes was developed and tested. These new membranes ranged from 250 to 5000 angstroms in thickness (1×10^{-6} to 2×10^{-5} inch) and consisted of esters, ethers, and mixed esters and ethers of polysaccharides (primarily cellulose). In previous research efforts in water desalination, these membranes have provided water fluxes up to 35 gfd at 97-percent salt rejection (after 1200 hours of testing under 800-psi pressure, at one percent sodium chloride feed and 25°C).[1] The ultrathin membrane was supported by a microporous support film developed at North Star Research and Development Institute, that had high chemical resistance and strength. The composite system of membrane and support has been successfully applied to tubular configurations, and *in situ* replacement of the ultrathin desalination film has been shown feasible.[1, 2] This approach toward the treatment of municipal wastewaters by reverse osmosis offers the possibility of high reverse osmosis performance and low cost.

The objective of the program reported here was to develop promising new membrane candidates for municipal waste treatment by reverse osmosis. This first phase has included the synthesis, fabrication, and screening of new and ultrathin membranes for effective reverse osmosis performance. A high-performing membrane would exhibit high water flux, adequate rejection of undesirable species, and low flux decline. The approach toward accomplishing this objective was two-fold:

- Initial screening of the membranes by running short reverse osmosis tests using sodium chloride. Salt rejections below 50 percent or water fluxes below 20 gfd were generally considered not acceptable.

- Reverse osmosis testing of the more promising membranes from the salt-solution screening using secondary effluent from a municipal sewage treatment plant. Along with water flux, the rejections of the following species were measured: total dissolved solids (TDS), ammonia, organics after filtration as total organic carbon (TOC), and soluble phosphates. Flux declines were observed on the best membrane candidates for extended time periods.

This report summarizes the results of the screening program, with emphasis on the most successful new membrane candidates for reverse osmosis treatment of municipal wastewaters.

EXPERIMENTAL

The experimental effort for this program included polymer preparation, preparation of ultrathin membranes and support film, and testing reverse osmosis performance. The general experimental procedures are summarized below, with pertinent descriptions of equipment and apparatus.

Polymer Preparation

Structure

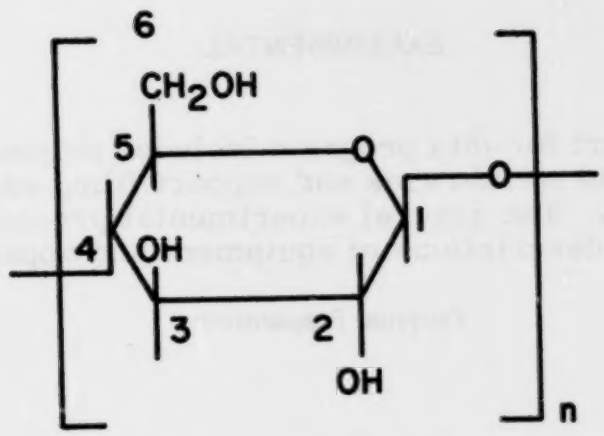
The basic repeating structure of cellulose is shown in Figure 1. The polymers used in this program are formed by substituting esters or ethers for the hydrogen atoms on the hydroxyl groups associated with the 2, 3, and 6 positions on the ring. The degree of substitution (DS) is therefore three, at maximum substitution. For example, for the ester derivative cellulose acetate, E 398-10, the acetate ester groups comprise an average of 2.4 of the available sites (DS for acetate = 2.4), and the remaining 0.6 site is the hydroxyl (-OH) group (DS for hydroxyl = 0.6). The structure of the basic repeating unit of β-glucan, another polysaccharide used in this work, is given in Figure 2. The same substitutions at the 2, 3, and 6 positions as cellulose are possible for β-glucan.

Transport properties of materials across polysaccharide membranes are grossly affected by substitution of functional groups (*e.g.*, esters and ethers at the positions indicated in Figure 1).[2, 3, 4] Polysaccharide derivatives with a high degree of substitution of ester groups, and, in addition, a minor proportion of highly hydrophylic substituent, were considered desirable. The type of hydrophylic substituent was varied both in charge (acidic, basic, or neutral) and in the relative strength of the acid or basic groups.

Preparation Procedures

The procedure for the preparation of the polysaccharide derivatives followed two basic techniques:

- The starting material was cellulose acetate with free hydroxyl groups (that is, a DS of less than three for acetyl). The cellulose acetate was then reacted with a suitable hydrophylic reagent to produce the desired derivative for film casting. Completion of the reaction was determined in the product from the infrared absorption of a 1-mil film at 3500 cm^{-1} (absence of the hydroxyl absorption peak indicates complete substitution). The substitution of the new group was then estimated by subtraction of the known acetyl content from 3.0.



The chain structure may be represented as:

$$G\underset{\beta\,(1 \rightarrow 4)}{\text{———}}\ G\underset{\beta\,(1 \rightarrow 4)}{\text{———}}\ G - - - -$$

where:

G = anhydroglucose unit

Cellulose ester:

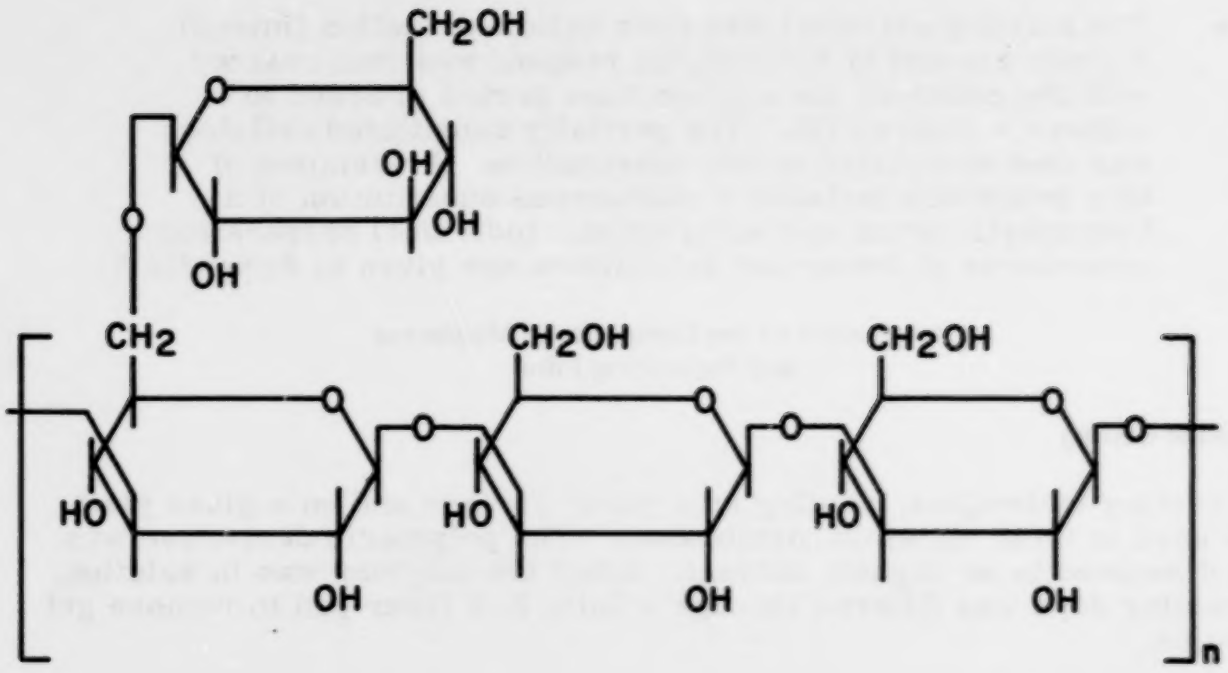
H atom on the hydroxyl groups associated with the 2, 3, or 6 position substituted by ester group; for example, acetate $\left(\begin{matrix} O - C - CH_3 \\ \| \\ O \end{matrix}\right)$

Cellulose ether:

H atom on the hydroxyl group associated with the 2, 3, or 6 position substituted by ether group; for example, methyl sulfonate:

$$\left(\begin{matrix} O \\ \| \\ O - S - CH_3 \\ \| \\ O \end{matrix}\right)$$

Figure 1. Structure of Cellulose



All glucose units are linked beta (1→3) in the chain skeleton and beta (1→6) in the appended glucose units. The chain structure may be represented as:

$$\begin{array}{l} G \\ | \\ G \end{array} \underset{\beta(1\rightarrow 3)}{\overset{\beta(1\rightarrow 6)}{\text{———}}} G \underset{\beta(1\rightarrow 3)}{\text{———}} G \underset{\beta(1\rightarrow 3)}{\text{———}} \begin{array}{l} G \\ | \\ G \end{array} \underset{\beta(1\rightarrow 3)}{\overset{\beta(1\rightarrow 6)}{\text{———}}} G - - -$$

where:

G = anhydroglucose unit

Ester and ether derivatives: substitution for some H atoms as in Figure 1.

Figure 2. Structure of β-Glucan

- The starting material was pure cellulose (cotton linters). A given amount of hydrophylic reagent was then reacted with the cellulose for a given time period in order to achieve a desired DS. The partially substituted cellulose was then acetylated to full substitution. A variation of this procedure included simultaneous substitution of a hydrophylic agent and acetylation. Individual preparation procedures of important derivatives are given in Appendix A.

Preparation of the Composite of Membrane and Supporting Film

Membrane Casting

Two casting techniques, casting on a water surface and on a glass plate, were used to form ultrathin membranes. The polymeric derivative was first dissolved in an organic solvent. After the polymer was in solution, the casting dope was filtered through a Seitz K-5 filter pad to remove gel particles.

Casting on a Water Surface. The solution with up to five percent by weight polymer was poured onto a water surface. The solution spread quickly and gelled to form an ultrathin membrane. The thickness was controlled by pulling the gelling membrane across the water surface at a constant rate.[5] The solvents included cyclohexanone or a 90:10 mixture of dichloromethane: methanol. Most of the ultrathin membranes were formed by this technique.

Casting on a Glass Plate. A 2-mil Gardner knife was used to draw the casting solution across a glass plate. The membrane was then formed by evaporation of the solvent at ambient conditions in a clean-air hood. This method was used for a few polymers that could not be cast on water. These membranes, at about 10,000 Å in thickness, were always thicker than the membranes cast on water.

Membrane Thickness

The thicknesses of the membranes were measured on a Reichert Metallograph equipped with a Nomarski polarization interferometer.[6]

Membrane Support

Either a Millipore VFWP filter or a microporous polysulfone film was used as a support for the ultrathin membranes in the reverse osmosis tests. The preparation procedure for the polysulfone film is described elsewhere.[2, 6] The support was laminated to the ultrathin membrane by immersing the support in the water underneath the ultrathin membrane and pulling it out of the water with the ultrathin membrane on its surface.

Reverse Osmosis Testing

All the tests were performed with the membrane-support composite placed in a flat circular test cell. The cell is shown in Figure 3, with the key dimensions of channel height and diameter indicated. The membranes were tested in a recirculating (constant feed concentration) system shown in Figure 4, with provision for testing four membranes at one time. In addition to the four reverse osmosis cells, the test loop contained a five-gallon brine reservoir, a Model 241-144B Milton Roy pump, an accumulator, a heat exchanger, a needle valve for system pressure control, a 100-mesh high-pressure filter, a rotameter, and a five-micron Cuno filter.

The general conditions for the reverse osmosis measurements with sodium chloride and secondary effluent are given in Table 1. The feed flow rate of 3500 ml/min produces a velocity adequate to control concentration polarization.[7] Biebrich scarlet dye was always added to the salt solution to confirm that no pinholes were present.

Each membrane underwent twenty hours of reverse osmosis testing with the sodium chloride feed. If this initial screening test looked promising, the membrane was then tested with secondary effluent.

For all the reverse osmosis tests, water flux was obtained by timing the upward movement of the water meniscus in a 10-ml pipette. The product-water flow rate in ml/min was multiplied by the conversion factor for these cells of 21.2 to obtain gallons per square foot per day (gfd). In the case of the salt solution screening tests, the percent rejection of salt was calculated from the salt concentrations in the feed and the product as determined from conductivity measurements.

For secondary effluent the constituents for which the feed and product water were analyzed included total organic carbon (TOC), ammonia nitrogen, nitrate nitrogen, orthophosphate, suspended solids, and dissolved solids. Except for suspended solids, the feed was filtered with a 0.45-micron filter before analysis. The analytical procedures and any procedural modifications are described briefly and referenced in Appendix B.

Secondary Effluent Feed

The feed for the secondary effluent tests was obtained from the Minneapolis-St. Paul Sanitary District plant. This plant has a high-rate activated sludge process designed for 75-percent removal of biochemical oxygen demand (BOD). Average analytical data on the raw, primary, and secondary effluents for a typical month are given in Table 2. To prevent excessive biological activity before reverse osmosis testing, the secondary effluent feed was stored at 4°C.

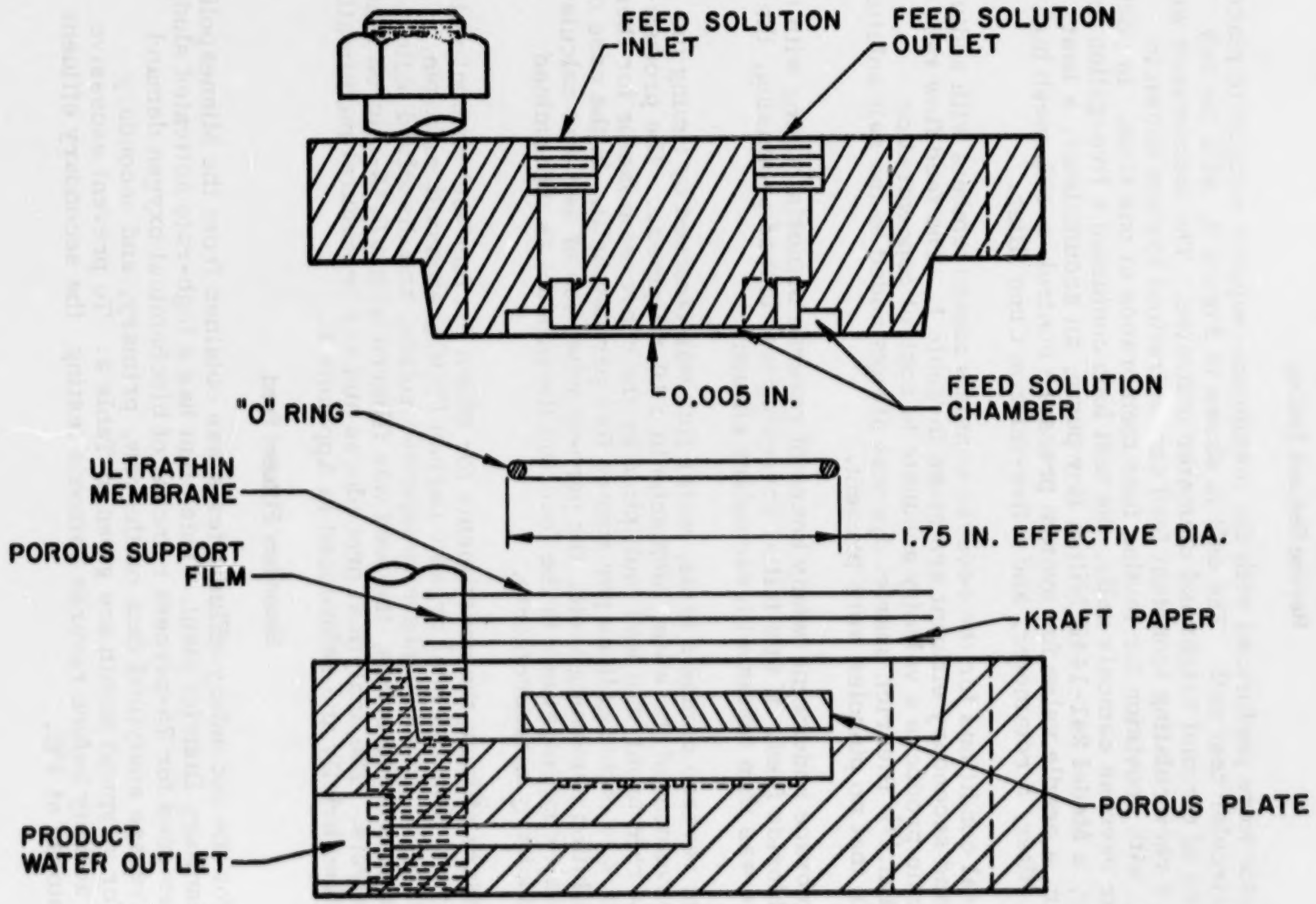


Figure 3. Dynamic Cell for Reverse Osmosis

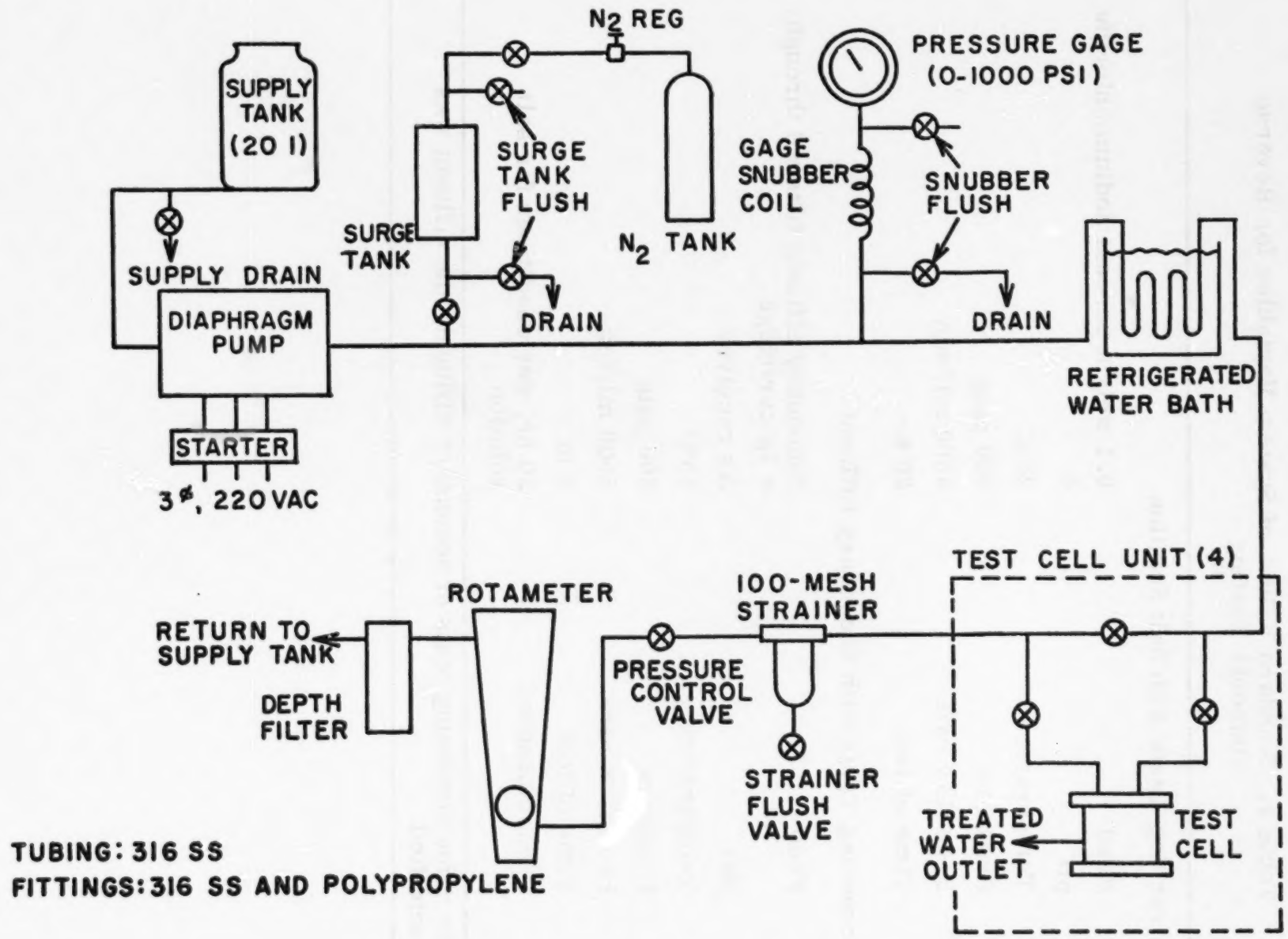


Figure 4. Schematic Diagram of Reverse Osmosis Test Apparatus

Table 1. Standard Values of System Variables for Reverse Osmosis Testing

Screening Tests with Salt Solution	
Feed	0.1 weight percent sodium chloride
pH	7
Temperature	25°C
Pressure	600 psig
Feed flow rate	3500 ml/min
Time of test	20 hr
Screening Tests with Secondary Effluent	
Feed	Secondary effluent filtered through a 1μ cartridge
pH*	As received
Temperature	25°C
Pressure	600 psig
Feed flow rate	3500 ml/min
Time of test	6 hr
Precompressed	20 hr, per conditions for salt solution

*In some screening tests of secondary effluent, the effluent was acidified.

Table 2. Minneapolis-St. Paul Sanitary District Wastewater Data*

	Raw**	Primary	Secondary
Chemical Oxygen Demand (COD)(mg/1)	370-520	290-430	190-220
Biochemical Oxygen Demand (BOD)(mg/1)	222	167	56
Ammonia – N (mg/1)	4-12	4-12	4-7
Kjeldahl N (mg/1)	19-24	18-23	9-15
Phosphate (mg/1)	7-19	7-18	6-15
Total Suspended Solids (mg/1)	291	117	49
Total Dissolved Solids (mg/1)	604	606	566
Chloride (mg/1)	83-99	75-98	59-98
Dissolved Oxygen (mg/1)	0.40	0.42	2.6
Temperature (°F)	70	70	–
pH	7.3	7.3	7.4
Soluble Organics (mg/1)	–	–	58†

*Permission for use granted by the District, April 1970.
**Single figures = average for July 1969.
Range figures = data from 1967-1968.
†Measured at North Star.

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RESULTS

The experimental work included the four following major efforts:

1. Membrane screening to determine the most effective polymer.

2. A brief look at major effluent variables and their effect on reverse osmosis performance.

3. Preliminary optimization of the best membrane candidates to define the important optimization variables and improve performance.

4. Some extended-time testing of the best membrane candidates to evaluate their long-term performance.

In addition, a preliminary economic analysis was carried out on some of the new polymer materials. Important data, their interpretation, and conclusions are summarized and presented below.

Forty-four polymers were tested in the reverse osmosis cell for water flux and rejection using a 0.1-percent sodium chloride feed (in some early cases, a one-percent feed). The following membranes were tested for reverse osmosis performance using the secondary effluent feed (cellulose acetate is referred to as CA).

Anionic

CA sulfate

Cellulose methyl sulfonate O-propyl sulfonic acid

CA O-propyl sulfonic acid

CA adduct of methylol phenol

CA phosphate

CA phthalic acid half ester

Cationic

CA methylol morpholine adduct

CA pyrrolidone adduct

β-glucan acetate diamethylaminoethyl ether

Cationic-Anionic

CA pyridine dicarboxylic acid half ester

Nonionic

CA

CA methyl sulfonate

CA dimethyl sulfonate

Xylan acetate

Methyl CA

Methyl cellulose methyl sulfonate

Cellulose trimethyl sulfonate

CA propane sulfonate

β-glucan diacetate

The most promising new membranes were of the anionic type. The reason is not known at this time.

The salt-screening procedures saved a considerable amount of time in this membrane screening program. The membranes with salt rejections less than 50 percent or water fluxes less than 20 gfd were eliminated. In general, the salt rejections were found to be proportional to the secondary effluent rejections. One apparent exception, however, was the rejection of the dissolved organics; higher TOC rejections than expected were obtained using low-salt-rejecting membranes. Some typical salt-screening results are given in Table 3. Most of these membranes did not pass to the secondary effluent testing stage.

Most Promising Membranes

Of the 44 membranes of different polysaccharide derivatives screened, the following new polymers were found to exhibit outstanding reverse osmosis properties:

- Cellulose methyl sulfonate O-propyl sulfonic acid (CMSOPSA)
- Cellulose acetate O-propyl sulfonic acid (CAPOSA)
- Cellulose acetate phosphate
- Cellulose acetate adduct of methylol phenol

Table 3. Reverse Osmosis Performance of Representative Membranes with Sodium Chloride Solution

Conditions:
NaCl ..... 0.1 percent
Temperature ..... 25°C
Pressure ..... 600 psig
Support Film ..... Millipore VFWP Filter
Feed pH 7
Feed Flow Rate ..... 3500 ml/min

Polymer and Batch Number	Thickness (Å)	Flux after ~20 hr (gfd)	Salt Rejection (%)
Anionic			
Cellulose Acetate Sulfate (211-52A)	1600	13	84
Cellulose Acetate Phosphate (211-58B)	1400	31	72
Cationic			
β-glucan Acetate Dimethylaminoethyl Ether (211-40A)	2000	10	99
Cellulose Acetate Adduct of Dimethylol Piperazine (211-82B)	1600	66	52
Cellulose Acetate Diethanolamine Adduct (211-45A)	5900	48	28
Cellulose Acetate Ethyl Trimethyl Ammonium Chloride (211-71A)	1800	5	94
Nonionic			
β-glucan Diacetate (87-26A)	1800	14	94
Methyl Cellulose Methyl Sulfonate Acetate (211-64A)	1700	7	98
Cellulose Acetate Methyl Sulfonate (211-10C)	1300	14	97

Performance of these membranes is shown in Table 4. For purposes of comparison, a commercially available asymmetric cellulose acetate membrane is included in the table.

Two membranes looked particularly promising for both high flux and high rejection: cellulose acetate O-propyl sulfonic acid (CAOPSA) and cellulose methyl sulfonate O-propyl sulfonic acid (CMSOPSA). Both membranes exhibited high ammonia rejections (96 and 93 percent, respectively), adequate TOC rejections (89 and 93 percent, respectively), and high TDS rejections (96 and 95 percent, respectively). For practical purposes, the phosphate rejections were 100 percent. The rejection of nitrates was high for CAOPSA (93 percent), but lower for CMSOPSA (81 percent). The water flux through these membranes was above 40 gfd. Presumably, if the CMSOPSA membrane had been as thin as the CAOPSA membrane, CMSOPSA would have surpassed CAOPSA substantially in water flux.

The DS of both of these membranes for the propyl sulfonic acid substituent was estimated at less than 0.1. Increasing the DS of this functional group would increase the water flux of the membrane but decrease the rejection. The structures of these two polymers are given in Figure 5.

The cellulose acetate adduct of methylol phenol was included because of its high flux (64 gfd) and high TOC rejection (89 percent). Chemical and process optimization should improve its performance considerably.

The commercial cellulose acetate asymmetric membrane (RO-97) that was used for comparison in Table 4 exhibited generally adequate rejections but low water flux. Data on the reverse osmosis performance of ultrathin cellulose acetate is presented and discussed later in this report.

Effects of Effluent Properties

The water flux and salt rejection of membranes for municipal wastewater treatment are affected by operating variables such as temperature, pressure, feed pH, feed concentration, and effluent filtration. Temperature and pressure effects are well known, and were not studied in this program. The remaining variables were given brief consideration and, except for membrane cleaning (discussed later in this report), their effects on reverse osmosis performance are presented in this section.

Feed pH and Resistance of Membrane to Degradation

The pH of the feed affects the structural integrity of a polymeric membrane. For cellulose acetate, the optimum feed pH is between 5 and 6, where degradation by hydrolysis is minimal.[8] In addition to hydrolytic damage to the membranes, the feed pH can affect the molecular structure of the solution constituents as well as the ionic form of an anionic or cationic membrane. These latter effects can result in significant changes in reverse osmosis performance.

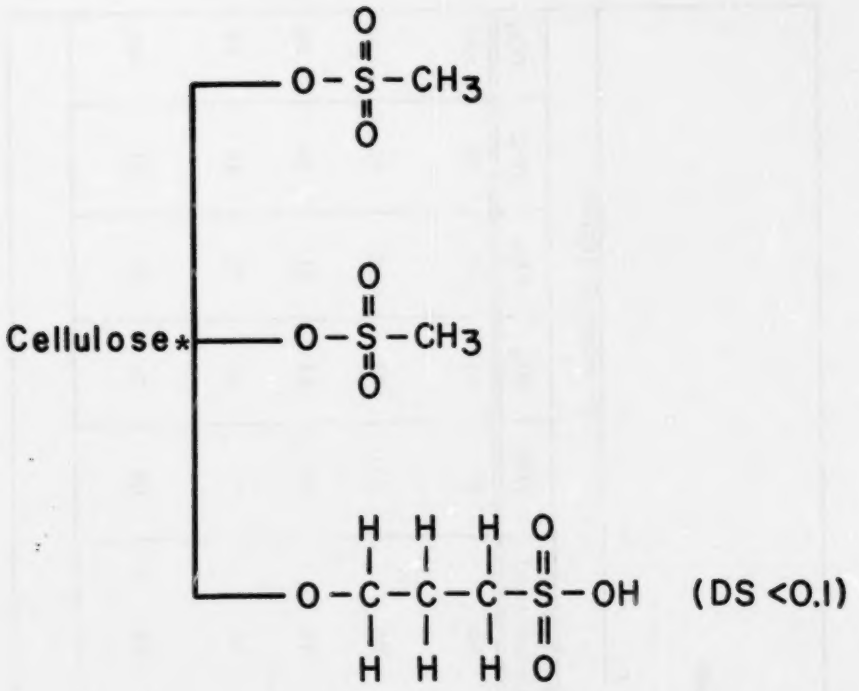
Table 4. Most Promising Candidate Polymers as Membranes for Municipal Waste Treatment by Reverse Osmosis

Conditions:
- Pressure ..... 600 psig
- Temperature ..... 25°C
- Effluent ..... Filtered Secondary Effluent
- Feed pH ..... ~7 for Salt Solution and 7-8 for Effluent
- Feed Flow Rate ..... 3500 ml/min
- Support Film ..... Millipore VFWP Filter

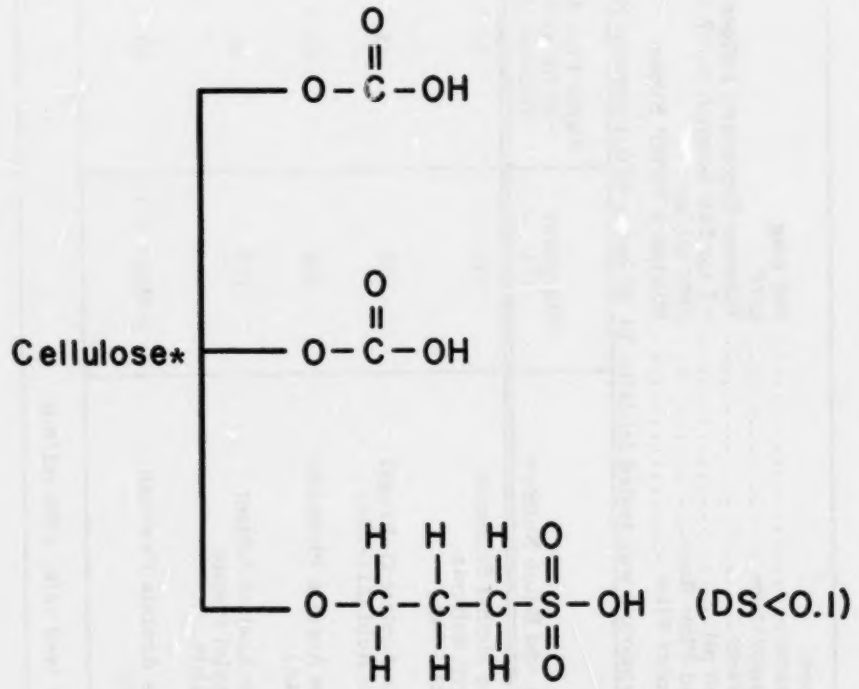
Each membrane was tested initially for 20 hours in 0.1 percent NaCl at pH 7

Polymer and Batch Number	Thickness (Å)	Water Flux After ~20 hr with Salt Solution (gfd)	Percentage Rejection					
			NaCl (with Salt Solution)	TDS	NO_3	NH_3	TOC	PO_4
Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-96A)	570	44	90	95	81	93	93	>99
Cellulose Acetate O-Propyl Sulfonic Acid (211-95A)	370	43	96	96	93	96	89	>99
Cellulose Acetate Phosphate (211-94A)	260	49	74	89	64	81	89	96
Cellulose Acetate Adduct of Methylol Phenol (211-83B)*	740	64	50	73	43	70	89	95
Cellulose Acetate Eastman (RO-97)*	Asymmetric	20	96	96	74	96	94	>99

*Effluent feed rate, 1000 ml/min.



A. Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid



B. Cellulose Acetate O-Propyl Sulfonic Acid

*Substitutions on the 2, 3, and 6 positions of cellulose (Figure 1).

Figure 5. Polymer Structure

The effect of high pH on the reverse osmosis performance of CMSOPSA membranes was shown to be significantly less than on that of cellulose acetate. For cellulose acetate, hydrolysis in acidic or basic solution results in removal of the acetate groups and subsequent poor rejection. An experiment with CMSOPSA (211-89A) and cellulose acetate (E 398-10) using a sodium chloride solution at pH = 11, showed that the reverse osmosis performance of the CMSOPSA membrane deteriorated much less than that of the cellulose acetate. The salt rejection of the cellulose acetate membrane was 18 percent, and that of CMSOPSA was 90 percent, after twenty hours of testing. CMSOPSA may also deteriorate slower than cellulose acetate under the less extreme pH conditions for municipal waste effluents.

Feed Concentration

A test was conducted to determine the effect of feed concentration on the rejection performance of a membrane. In the test, the sodium chloride concentration of a salt solution feed was increased from 500 mg/l to 5000 mg/l to simulate the concentration range occurring in a reverse osmosis unit during treatment of an effluent. As expected, there was no effect on the rejection performance of cellulose acetate (RO-89). The salt rejection of a CMSOPSA (211-89A) membrane decreased only slightly, from 96 to 95 percent. Some decrease could be expected because of the existence of some ion exchange character in this derivative.(9)

Preliminary Membrane Optimization

The reverse osmosis performance of a membrane can be improved to a considerable extent by modifications in its fabrication process. The membrane variables that can be modified for obtaining high water fluxes, high rejections, and low flux declines include:

- Polymer preparation process and DS
- Casting conditions
- Type of support film for ultrathin membranes
- Membrane annealing conditions
- Membrane thickness

Controlling the effects of the above variables would improve the performance of the membrane/support composite for optimum treatment of municipal wastewaters. A preliminary optimization study was carried out on the more promising membranes, CMSOPSA, CAOPSA, and cellulose acetate. Since the flux and rejection of membranes with a sodium chloride feed has been shown to be roughly the same as the unfouled flux and TDS rejection of a secondary effluent feed, and because a greater number of experiments can be carried out in a given time period with sodium chloride, the 0.1-percent sodium chloride feed was used under the conditions in Table 1.

Polymer Preparation and Degree of Substitution

Table 5 illustrates the results obtained from different batches of CMSOPSA. The membranes listed were prepared from three different batches: (1) the original batch (211-89A); (2) a duplicate batch (211-96A); and a third batch (211-96B), that was prepared with a higher DS for O-propyl sulfonic acid to obtain higher water flux. The results are summarized below.

1. Batch 211-89A was the original preparation. Membrane 3 was cast from the same polymer solution as membranes 1 and 2, but one month later. It was cast very thin (280Å) to achieve a high water flux. This membrane exhibited the same salt rejection as membranes 1 and 2, but with only slightly greater water flux. The unexpectedly low water flux could be due to polymer solution changes during the one-month period, producing a tighter membrane. Thus, the storage of polymer solutions must be considered in an optimization study.

2. Batch 211-96A was prepared with approximately the same reaction conditions used previously for Batch 211-89A cited above. Membrane 4 cast from Batch 211-96A did not exactly reproduce any results of membranes 1, 2, and 3.

3. Batch 211-96B was prepared with reaction conditions adjusted to obtain a product with a higher DS of O-propyl sulfonic acid. Membrane 5 formed from this batch had a higher water flux and a lower salt rejection than membranes 1, 2, 3, and 4. This is the expected behavior for a polymer more highly substituted with flux-promoting substituents.

These results indicate that, at present, it is difficult to prepare a polymer with predictable properties, and thus the reaction conditions must be rigorously controlled in an optimization study. Investigation and study of the reaction conditions were not within the goals of this screening program.

Casting Conditions

Among the many casting conditions affecting the performance of the membrane, an interesting observation was made regarding the type of solvent used. It was found that some polymer-solvent solutions gave membranes that were cloudy in appearance, even though the solution appearance indicated good polymer solubility. The cloudy-appearing membranes exhibited higher flux, but lower salt rejection, than the normal transparent membranes. These cloudy membranes probably contained voids or gel particles; however, the exact explanation for this behavior is not known. An example is given in Table 6.

Table 5. Effect of Polymer Preparation Procedure (Designated as Batch Number) on Water Flux and Salt Rejection for Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid

Conditions:
Pressure ..... 600 psig
Temperature ..... 25°C
Salt Solution ..... 0.1-percent NaCl
Feed pH 7
Feed Flow Rate ..... 3500 ml/min
Support Film ..... Millipore VFWP Filter

Membrane Number	Batch Number	Thickness (Å)	Water Flux After 20 hr (gfd)	Percentage Rejection
1	211-89A	1300	37	94
2	211-89A	1200	30	95
3	211-89A	280	40	95
4	211-96A	570	44	90
5	211-96B	1200	66	75

Table 6. Effect of Casting Solvent on Reverse Osmosis Performance of Cellulose Acetate O-Propyl Sulfonic Acid (211-63A)

Solvent(s)	Membrane Appearance	Thickness (Å)	Flux (gfd)	Percentage Salt Rejection
Cyclohexanone	Cloudy	2000	37	54
Dichloromethane/ methanol	Transparent	1800	26	96

Type of Support Film

Millipore VFWP filters were used for supporting ultrathin membranes during the early part of this program. More suitable microporous support films made from polysulfone have been developed at North Star Research and Development Institute for supporting ultrathin membranes and are presently used for the supports for tubular ultrathin membranes.[6, 2] To determine optimum performance of the composite in long-term tests, the two supports were compared for their effects on water flux and flux decline.

Effect on Water Flux at Low Membrane Thicknesses. High fluxes can be obtained by use of the polysulfone support film rather than a Millipore support film. Figure 6 shows the effect of the support on the water flux/ thickness relationship of two ultrathin membranes.

The use of Millipore or polysulfone supports caused no difference in flux at high thicknesses for both membranes. However, thinner membranes, which are necessary to achieve higher fluxes, require the use of polysulfone supports to attain these higher fluxes. Polysulfone enhanced the flux of cellulose acetate (E 398-10) membranes to below 500 to 700 angstroms in thickness. Polysulfone supports were necessary to attain high flux for CMSOPSA (211-96B) membranes below 2000 angstroms in thickness. The polysulfone sheets have smaller, more uniformally sized and a larger number of pores than Millipore filters.[1] We believe that these pore properties contribute toward the superior support behavior of the polysulfone. Further research will be necessary, however, to determine the exact reasons for the improved support properties of polysulfone.

Effect on Flux Decline. Lower flux declines can be realized by using the polysulfone support film. Flux-decline values from the slopes of logarithmic plots of flux versus time for cellulose acetate and CMSOPSA membranes on both supports are given in Table 7.

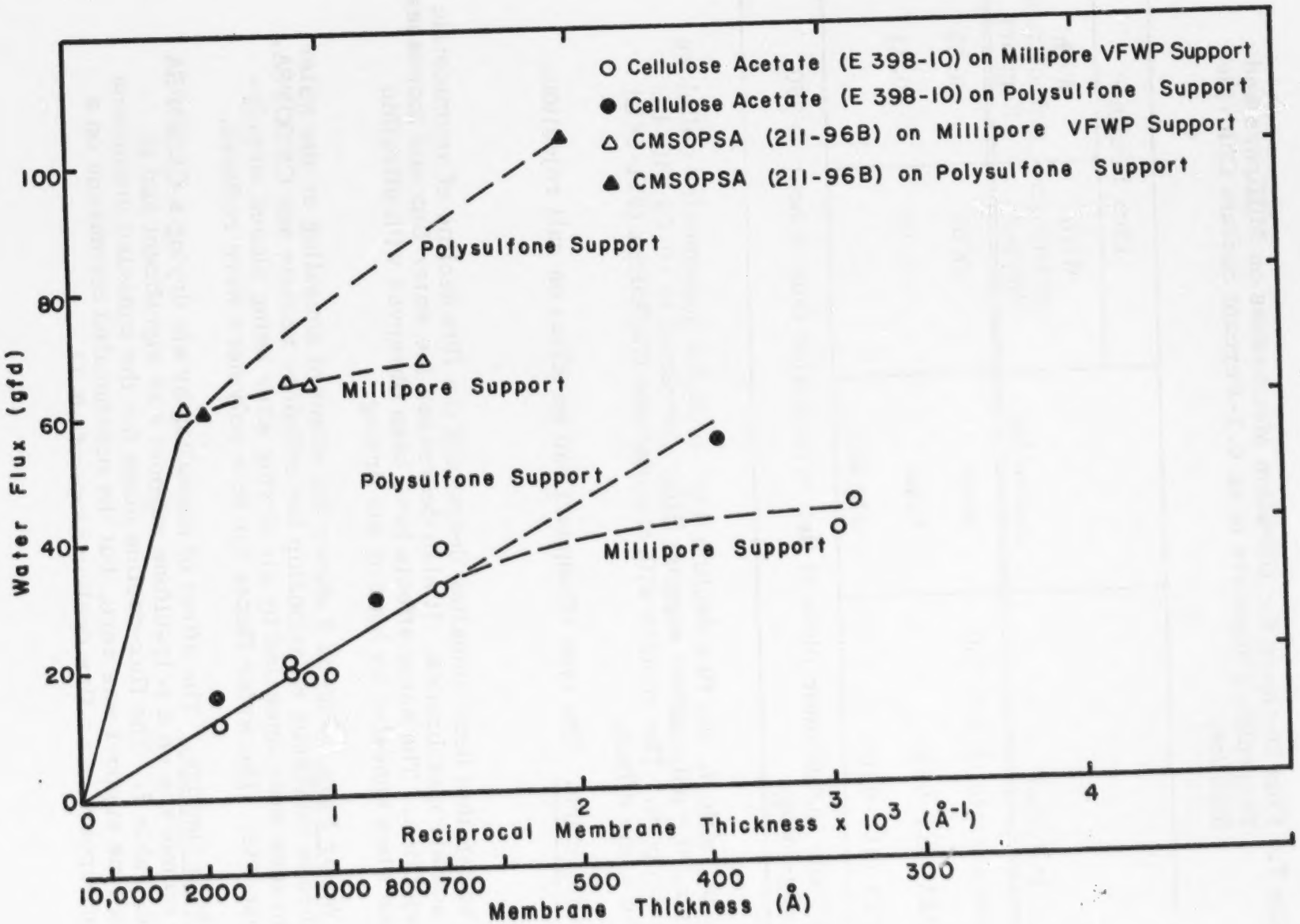


Figure 6. Water Flux as a Function of Membrane Thickness: Effect of Support Film

Table 7. Flux Declines for Ultrathin Membranes on Millipore and Polysulfone Supports in an 0.1-Percent Sodium Chloride Solution

Polymer	Annealing	Flux Decline*	
		With Millipore Support	With Polysulfone Support
Cellulose acetate (E 398-10)	None	-0.08	-0.05
CMSOPSA (211-96B)	None	-0.14	-0.11
CMSOPSA (211-96B)	Air Dry	–	0

*Slopes from logarithmic plots of flux versus time from 1 hour to 260 hours of testing.

As shown in Table 7, the flux decline was -0.05 for nonannealed cellulose acetate using the polysulfone support film, compared to -0.08 with the Millipore support. The results with nonannealed CMSOPSA (211-96B) showed the same effect.

Effect on Rejection. The type of support had no effect on salt rejection.

Annealing

It is well known that heat annealing decreases the flux decline of asymmetric cellulose acetate membranes. It also decreases the water flux and increases the salt rejection. The same effects have been observed with ultrathin membranes when annealed by heat or air drying.

Effect on Water Flux. Figure 7 shows the effect of annealing on the water flux/membrane thickness relationship for cellulose acetate and CMSOPSA. The membranes were annealed by air drying after being placed on polysulfone supports. The water fluxes for both polymers were reduced.

Effect on Flux Decline. The effect of annealing by air drying a CMSOPSA (211-96B) membrane on a polysulfone support was significant and is indicated in Table 7. The flux-decline slope for the annealed membrane on a polysulfone support was zero, but the nonannealed membrane on a polysulfone support has a flux decline slope of -0.11.

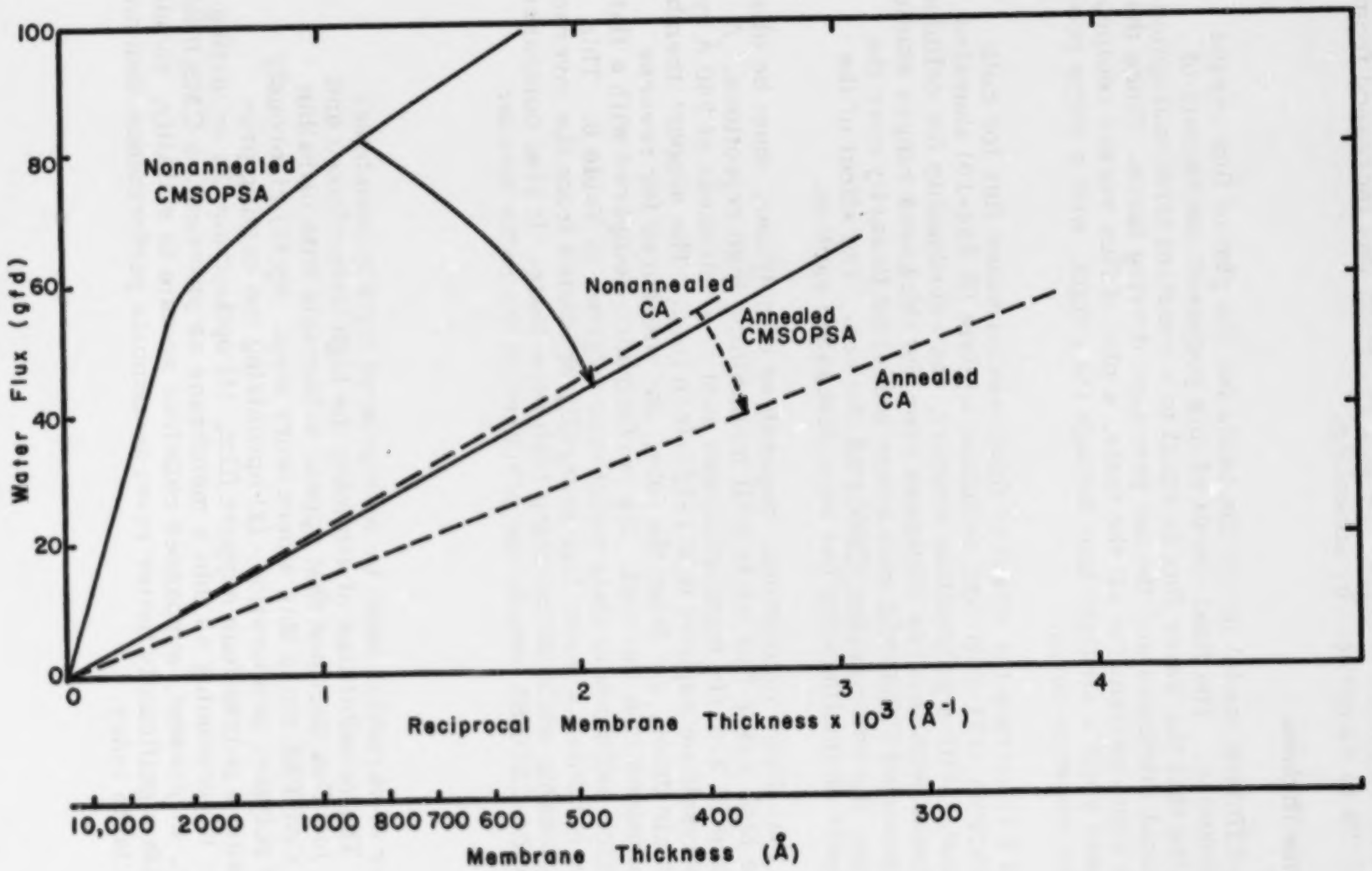


Figure 7. Water Flux as a Function of Membrane Thickness: Effect of Annealing

Effect on Salt Rejection. Annealing increased the salt rejection of the CMSOPSA membranes from approximately 70 percent (for nonannealed) to 94 percent. For cellulose acetate, the salt rejection was increased from approximately 92 to 95 percent by annealing.

Effect of Membrane Thickness

The solution-diffusion model forms the basis for the plot of flux versus reciprocal thickness. The final result of this proposed mechanism of transport states that the water flux is equal to a constant term multiplied by the reciprocal thickness and the net pressure driving force. Since the pressure was kept constant for all the tests, a plot of flux versus reciprocal thickness should yield a straight line through the origin, with a slope proportional to the constant term.

Figures 6 and 7 illustrate the effect of thickness on water flux for both polymers CMSOPSA (211-96B) and cellulose acetate (E 398-10) annealed and nonannealed. With a polysulfone support, the relationship for cellulose acetate was linear with inverse thickness over the thickness ranges studied. Although the annealed CMSOPSA membrane exhibited linearity over the thickness range, the nonannealed CMSOPSA did not. The effect of the Millipore support on nonlinearity has been discussed earlier.

It is apparent that these membranes, regardless of polymer, must be ultrathin to achieve high water flux while still maintaining high rejections. A cellulose acetate (E 398-10) membrane was cast at a thickness of 260 Å by casting on a polysulfone support in a 1-1/4-inch tube. The support/membrane composite was air dried, cut from the tube, and measured for reverse osmosis performance in a flat cell. Its performance compared with a flat-cast 2100-Å-thick cellulose acetate membrane is given in Table 8. This thin membrane exhibited a water flux generally predicted from the inverse thickness relationship while maintaining high rejections. It also compares favorably with the CAOPSA membrane prepared in the same manner (Table 3).

Conclusions

A large number of variables must be manipulated for any membrane optimization. The possibilities of attaining the high water fluxes and rejections and low flux declines that appear achievable with ultrathin CMSOPSA and CAOPSA make this a necessary step. By (1) rigorously controlling the polymer preparation, (2) optimizing the casting procedures, (3) using a polysulfone support film, (4) optimizing the annealing conditions, and (5) producing as thin a membrane as practical, a CMSOPSA membrane that, at present, surpasses cellulose acetate in stability, should be produced with significantly better reverse osmosis performance than any membrane available today.

Table 8. Effect of Thickness on Reverse Osmosis Properties of Cellulose Acetate (E 398-10) in Salt and Secondary Effluent

Conditions:
Pressure ..... 600 psig
Temperature ..... 25°C
Salt Solution ..... 0.1-percent NaCl
Effluent ..... Filtered Secondary Effluent
Feed pH ..... ~7 for Salt Solution and 7-8 for Effluent
Feed Flow Rate ..... 3500 ml/min
Support Film ..... Millipore VFWP Filter

Thickness (Å)	Water Flux After ~20 hr with Salt Solution (gfd)	Percent Rejections					
		NaCl (with Salt Solution)	TDS	NO_3	NH_3	TOC	PO_4
2100	14	95	>99	82	90	92	>99
260*	47	93	95	89	88	93	>99

*Cast on polysulfone support in tube and air dried.

Extended Time Testing

In the screening studies, all the reverse osmosis tests with secondary effluent were carried out for six hours after a twenty-hour reverse osmosis test (precompression) with salt solution. To determine applicability to an actual municipal waste situation, it was necessary to determine the behavior of the membranes during testing of a longer duration. Reverse osmosis tests of approximately one week's duration were carried out on selected membranes, and preliminary information on long-term flux, flux decline, and rejections was obtained.

Experimental Conditions and Procedures

The experimental procedure consisted of circulating a fresh, filtered secondary effluent feed at 600 psig through the four flat test cells containing the membranes. After twenty hours, the membranes in the test cells were cleaned, deionized water was circulated through the cells briefly under 600 psig, and fresh, filtered secondary effluent was circulated through the cells under 600 psig again for twenty hours. These twenty-hour test cycles, with the cleaning and deionized water procedures, were repeated seven times (150 hours). Each cycle was designated as a "test section" and given a number.

A preliminary long-term test was run to establish the procedures for secondary effluent filtration and membrane cleaning. The most effective filtration medium was glass fiber mats.[10, 11] The total suspended solids in the secondary effluent was reduced from 52 to 15 mg/l. The cleaning procedure used after each twenty-hour test section in this test series consisted of circulating a solution of 20 g/gal. Biz in the cells for 1.5 hours.

The long-term tests provided information on average water flux, fouling flux decline, long-term flux decline, and rejection. The average water flux of a test section was found by dividing the area under the test section curve (flux versus time) by the time period (~20 hours). The fouling flux decline was the decrease in flux that occurred during each twenty-hour test section. The long-term average flux decline was the decrease of the average water flux values from the first to last test sections. The rejections measured were total dissolved solids, ammonia, and dissolved organics (measured as total organic carbon).

Observed Reverse Osmosis Properties

The four membranes tested are listed in Table 9, along with their initial salt rejection data. One of the most promising high-flux, high-rejecting, new ultrathin membranes, CMSOPSA, was used. Another new ultrathin membrane, cellulose acetate methyl sulfonate, was used because of its high salt rejection in the initial screening study (at a thickness of 1300 Å – Table 3). A thinner membrane would retain the high rejection, but increase

Table 9. Membrane Characterization for Long-Term Secondary Effluent Test

Conditions:

Cell	Flat
Solution	0.1-percent NaCl
Pressure	600 psig
Feed Flow Rate	3500 ml/min
Temperature	25°C
pH	7

Support for ultrathin membranes – polysulfone

All ultrathin membranes annealed by air drying

Polymer and Batch Number	Thickness (Å)	~20-hr Flux (gfd)	Salt Rejection (%)
CMSOPSA (211-89A)	210	55	94
Cellulose Acetate Methyl Sulfonate (211-10C)	440	42	94
Cellulose Acetate (E 398-10)	290	50	94
Cellulose Acetate (RO-97)	Asymmetric	16	96

the water flux compared to the membranes tested earlier. For comparison purposes, the asymmetric cellulose acetate membrane (RO-97) was chosen, because it is the tightest standard commercial membrane. As a further control, an ultrathin cellulose acetate membrane (E 398-10), which had salt rejections comparable to the other membranes, was used. During this test, all the ultrathin membranes were annealed by air drying to achieve higher rejection. The control membrane of cellulose acetate (RO-97) was used as received.

It was convenient to characterize the membranes by initial twenty-hour reverse osmosis tests with sodium chloride. These tests also served as a "quality control" for the membranes to be used. Also, the twenty-hour flux compacted the membrane and eliminated further flux decline due to membrane compression during the long-term test. In Table 9, the water fluxes at the end of twenty hours varied between 42 and 55 for the ultrathin membranes and under 20 for the asymmetric membrane. Salt rejections for all the membranes were in the 95-percent range.

The experimental results are summarized in Table 10. The ultrathin cellulose acetate membrane apparently developed a defect at the beginning of the fourth test section (after 60 hours of testing). At the beginning of the fourth test section, the initial water flux was abnormally high (67 gfd) and the rejections had decreased significantly (e.g., conductivity rejection from 96 percent to 85 percent). The data for this membrane are thus given only for the first sixty hours of testing.

The specific results for important reverse osmosis parameters are summarized below.

- Average Water Fluxes

  The highest average water flux – 43 gfd – was observed for the CMSOPSA membrane in the first test section. After forty hours, the average water flux for this membrane remained at about 36 gfd for the remainder of the test (150 hours). The cellulose acetate ultrathin membrane exhibited an average flux of 34 gfd in the third test section. For both of these membranes, the actual water fluxes from the effluent varied from 54 gfd to 30 gfd. Much lower average fluxes were observed for the cellulose acetate methyl sulfonate and the asymmetric cellulose acetate control membrane (20 gfd and 13 gfd, respectively, over the last two-thirds of the test).

- Fouling Flux Decline

  The flux-versus-time data for two of the membranes are given in Figures 8 and 9. In Figure 8 for the CMSOPSA membrane, the initial water flux from the effluent in each

Table 10. Long-Term Secondary Effluent Test Results

Conditions:

Cell	Flat
Pressure	600 psig
Feed flow rate	3500 ml/min
Temperature	25°C
Secondary effluent pretreatment	Filtered through glass fiber mat and pH adjusted to 5
Periodic cleaning procedure	20 gm Biz/gal. water at 0 psig and 25°C circulated for 1.5 hr every 20 hr during test

Membrane	Deionized Water Flux (gfd)		Average Water Flux Within Test Section (gfd)							Average Percentage Rejection			Final Percent Salt Rejection
	Initial	Final	1	2	3	4	5	6	7	TDS	NH_3	TOC	
CMSOPSA (211-89A)	54	42	43	40	35	36	36	34	36	96	94	83	95
Cellulose Acetate Methyl Sulfonate (211-10C)	37	22	30	24	20	21	21	18	19	97	96	85	96
Cellulose Acetate (E 398-10)*	50	–	39	37	34	–	–	–	–	93	92	83	–
Cellulose Acetate (RO-97)	16	13	14.5	13.5	13.5	13.2	13.2	13.2	13.2	96	92	85	96

*An apparent membrane failure was observed after Test Section 3; the average rejections include only Test Sections 1, 2, and 3.

Feed Data [Average Concentration in Filtered Feed (mg/l)]			
TSS**	TDS	$NH_3(N)$	TOC
15	668	8.1	25.1

**TSS = 52 for unfiltered feed.

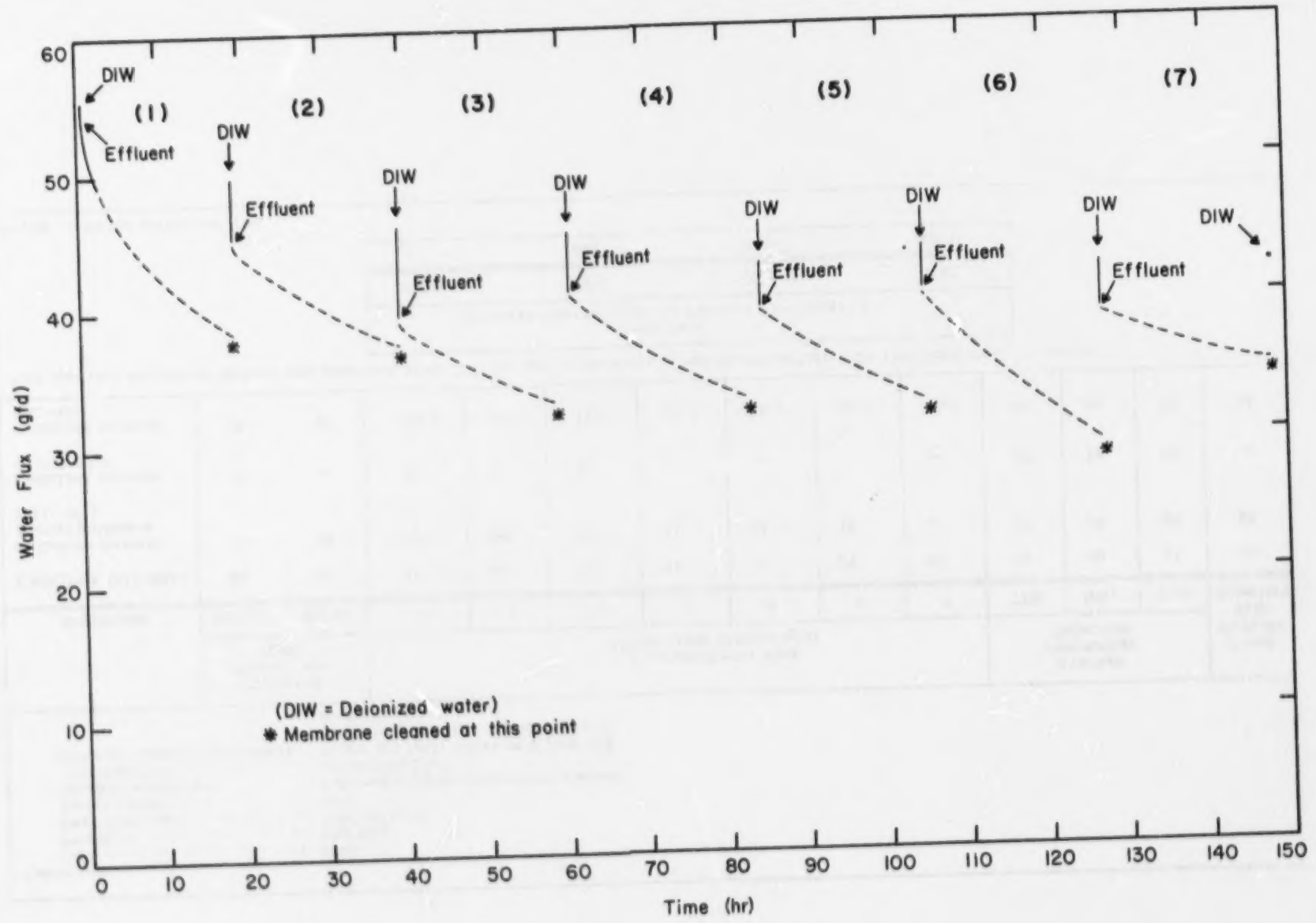


Figure 8. Water Flux Data from Secondary Effluent Test with Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid

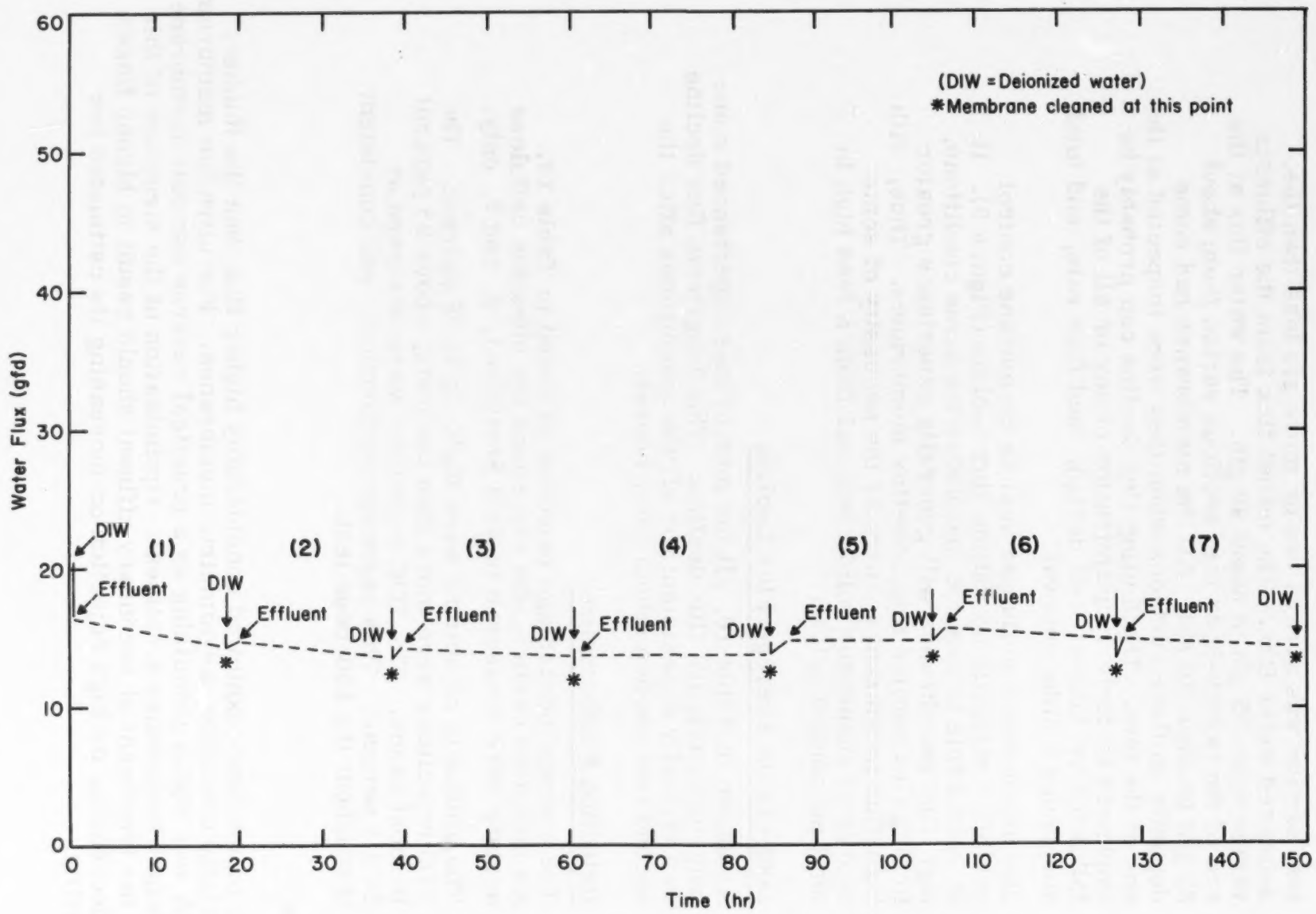


Figure 9. Water Flux Data from Secondary Effluent Test with Commercial Acetate Asymmetric Membrane

test section was always two or more gfd less than the deionized water flux. The initial flux from the effluents varied from 55 gfd to about 40 gfd. The water flux at the end of the twenty-hour test sections varied from about 38 gfd to about 30 gfd. All the membranes had some deposits on their surfaces when they were inspected at the end of the test. The fouling flux decline can probably be improved by further optimization of any or all of the following variables: cell design, feed flow rate, and total suspended solids removal.

The asymmetric cellulose acetate membrane control exhibited virtually no fouling flux decline (Figure 9). It is reasonable to assume that under the same conditions, high-flux membranes will generally experience greater fouling flux decline than low-flux membranes. Thus, with high-flux membranes, there is the necessity of some degree of suspended solids removal from a feed high in total suspended solids.

- Long-Term Average Flux Decline

As shown in Table 10, all the membranes experienced some long-term average flux decline. This long-term flux decline was virtually nonexistent for all the membranes after the second test section (about forty hours).

- Rejection Performance

The average percentage rejection is listed in Table 10. As indicated earlier, the rejections for ultrathin cellulose acetate were measured in Test Sections 1, 2, and 3, only.

The ammonia rejections were high, up to 96 percent. The TDS rejections were more than adequate, above 95 percent in most cases. The TOC rejections were observed at 84 ± 1 percent. This rejection performance was consistent throughout the 150-hour test.

Conclusions

Ultrathin membranes exhibited considerably higher flux than the thicker, commercially available, asymmetric membranes. For ultrathin membranes, CMSOPSA was highly promising as a practical reverse osmosis membrane for municipal wastewater treatment. Optimization of the structure of this polymer for treatment of secondary effluent should result in higher fluxes without decreasing its high rejection or increasing its estimated low degradability.

Preliminary Economic Analysis of Production Costs Of Tubular Ultrathin Membrane/Support Composites

An economic analysis was made of process costs relating to production of commercial quantities of ultrathin membrane/support composites for reverse osmosis water desalination. This analysis did not include the costs for the mechanical support tube, such as a fiber glass epoxy tube. A modified Zevnik-Buchanan approach was used, which is based on process capacity, process complexity, functional units of the process, and the Nelson Refinery Construction Index. The final estimated selling price included a 25-percent return on investment after taxes. The procedures and data are given in Appendix C.

It is convenient to consider the tubular configuration because of its high potential practicality in this application. The system of polysulfone support liner and ultrathin membrane looks promising from a production cost viewpoint. At a production capacity of 10 million tubes (one square foot of membrane per tube) per year, the estimated price for a polysulfone support liner and an ultrathin cellulose acetate membrane was 9.5 cents per tube. At a production capacity of one million tubes per year, the price was estimated to be 40 cents per tube.

One advantage of ultrathin membranes for reverse osmosis treatment of wastewater is their (cellulose acetate and possibly others) ability to be regenerated *in situ.* [2] Thus, the tube would not be discarded for membrane replacement. The replacement costs of the membrane, including all process and labor costs, would be somewhat less than the cost of the original membrane and liner, 8.3 cents per tube. If the membrane could be replaced five times the average cost for original membrane plus polysulfone support and the five replacement membranes would be 8.6 cents per tube.

Tubes with other ultrathin membranes, such as CMSOPSA, would have virtually the same cost as the combination of cellulose acetate and polysulfone given above. This would be true even if the cost of the new polymer were as high as $50 per pound (Appendix C). The reason why polymer cost has so little effect on total cost is the extremely small weight of polymer required for a square foot of membrane. Thus, the selling price is unchanged for all practical purposes when polymers with an approximately 100-fold raw material cost increase are used.

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APPENDIX A

Preparation Procedures of Pertinent Polymers

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APPENDIX A

PREPARATION PROCEDURES OF PERTINENT POLYMERS

Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-89A)

Ten grams of cotton linters (Hercules A-2000) were swelled in 100 g of 20-percent NaOH at -10°C for 24 hours. Three grams of propane sultone were blended with the wet fiber, using a spatula. The mixture was stirred occasionally for six hours, then allowed to stand at room temperature for four days. The etherified fiber was washed with methanol, 2-percent sulfuric acid, and glacial acetic acid.

The fiber was then dispersed in 250 ml of glacial acetic acid. Twenty grams of methyl sulfonic acid followed by 50 ml of acetic anhydride were added to produce a clear, thin solution within twenty minutes. The product was precipitated in 1.5 liters of deionized water containing 20 g of sodium acetate. The precipitate was mixed for 1/2 hour to decompose excess acetic anhydride, chopped in a Waring Blendor, washed, and dried at 100°C. The product (17 g) was soluble in hot cyclohexanone.

Cellulose Acetate O-Propyl Sulfonic Acid (211-95A)

Cotton linters (18 g of Hercules A-2000) were swelled in 100 g of 20-percent NaOH at -10°C for 24 hours. Propane sultone (3.0 g) was blended with the wet fiber, using a spatula. The mixture was stirred occasionally for six hours, then allowed to stand at room temperature for four days. The etherified fiber was washed with methanol, 2-percent sulfuric acid, and glacial acetic acid. The acetic acid wet fiber was diluted to 400 ml with acetic acid, and 20 g of 10-percent H_2SO_4 in acetic acid were added. The reaction proceeded rapidly, after addition of 100 ml of acetic anhydride, to give a clear solution in one hour. A mixture of 20 ml of water and 30 ml of acetic acid was added to decompose the excess acetic anhydride and sulfate ester, and mixing was continued 10 minutes. The solution was poured into two liters of deionized water containing 20 g of sodium acetate. The bulky precipitate was chopped in a Waring Blendor, filtered, washed, and dried at 80°C. The yield was 34 g, and the product was soluble in cyclohexanone.

Cellulose Acetate Phosphate (211-94A)

Eastman cellulose acetate 398-10 (10 g) was dried at 105°C and dissolved in 100 ml of reagent-grade pyridine. The solution was cooled in an ice bath, and 0.45 g of phosphorus oxychloride was added dropwise. After stirring 20 minutes, the viscosity of the solution began to increase, indicating cross-linking by the $POCl_3$. The reaction mixture was poured into 600 ml of deionized water at 10°C and stirred for 30 minutes. The product was dispersed in a Waring Blendor, filtered, washed, and air dried. The yield was 10.0 g.

Cellulose Acetate Adduct of Methylol Phenol (211-83B)

A ten-percent solution of methylol phenol in acetic acid was made by reacting 18.8 g of phenol (0.2 mole) with 6.0 g of paraformaldehyde (0.2 mole) in 163.2 g of acetic acid. Cotton linters (Hercules A-2000) were preactivated by soaking in water for 24 hours. The fiber was filtered and washed three times with glacial acetic acid. The acetic acid wet fiber was mixed with 200 g of glacial acetic acid and 10 g of 10-percent H_2SO_4 in acetic acid. The acetylation reaction was carried out by the addition of 50 ml of acetic anhydride. After one hour of reaction time, excess acetic anhydride and sulfate ester in the product were hydrolyzed by addition of 10 ml of water and 40 ml of acetic acid and mixing for 15 minutes. Fifty grams of the 10-percent methylol phenol solution was then added, and the product was precipitated in water, filtered, washed, and dried. The product (17 g) was soluble in cyclohexanone.

Cellulose Acetate Methyl Sulfonate (211-10C)

Ten grams of Eastman cellulose acetate 360-60 was dried at 105°C for two hours and dissolved in 140 ml of pyridine. After cooling the solution to -10°C, 10 g of methane sulfonyl chloride in pyridine was added in small portions. The solution was stirred for 24 hours at room temperature and precipitated into cold water. The precipitate was dispersed in the water in a Waring Blendor, filtered, and dried at 60°C. The product (13.0 g) was soluble in cyclohexanone and was estimated to have an acetyl DS of 2.1 and a methane sulfonate DS of 0.9.

APPENDIX B

Analytical Methods

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APPENDIX B

ANALYTICAL METHODS

Total Organic Carbon

Combustion-Infrared Analysis

American Society for Testing and Materials, D2579, Part 23 (1969)

This method covers the determination of organic carbon in the range from 2 to 150 mg/1 of carbon in water. The instrument used for the analysis was a Beckman Model 915 total organic carbon analyzer. The analysis required acid blowing of the samples prior to the organic carbon determination to remove all of the inorganic carbon. Microsamples of the acid-blown solutions were then injected into a heated catalytic packed tube in a stream of purified air. Organic matter was oxidized to carbon dioxide, which was measured by means of a nondispersive infrared stream analyzer.

Ammonia Nitrogen

Distillation and Titration

Association of Official Agricultural Chemists, 10th ed. (1965)

This method covers the determination of ammonia nitrogen in the range from 0.1 mg/1 to 20.0 mg/1 as nitrogen. The sample was transferred to a Wagner distillation apparatus and made alkaline with sodium hydroxide. The alkaline solution was distilled, and the freed ammonia was absorbed in boric acid and titrated.

Nitrate Nitrogen

Brucine Colorimetric Determination

Standard Methods for the Examination of Water and Wastewater, 12th ed. (1965)

This method covers the determination of nitrate nitrogen in the range of 0 to 11 mg/1 as nitrate. Brucine and nitrate react under acid conditions to form a sulfur-yellow color of intensity proportional to the original nitrate concentration. Photometric measurements were made on a Beckman Ratio Recording Spectrophotometer, DK-2A.

Orthophosphate

Photometric Amino Reduction Method

American Society for Testing and Materials, D-515, Part 23 (1969)

This method covers the determination of orthophosphate in the ranges from 0.5 to 20 mg/1 and from 0.1 to 1.0 mg/1 as phosphate. Orthophosphate reacts with ammonium molybdate in an acid medium to form a molybdophosphate, which, in turn, is reduced to a molybdenum-blue complex with aminonaphthol sulfonic acid. The color is proportional in intensity to the phosphate concentration. When a bizmuth salt is added to the sulfuric acid reagent, the intensity of the blue color increases fourfold. Photometric measurements were made on a Beckman Ratio Recording Spectrophotometer, DK-2A.

Total Suspended Solids

Filtration

Standard Methods for the Examination of Water and Wastewater, 12th ed. (1965)

Suspended matter is determined by the filtration of the sample through a 0.45-micron Millipore filter. The difference in the weight of the dried filter before and after filtration is the total weight of suspended solids in the sample.

Total Dissolved Solids

Evaporation

Standard Methods for the Examination of Water and Wastewater, 12th ed. (1965)

The sample is filtered through a 0.45-micron filter, and the filtrate evaporated in a weighed dish. The difference in the weight is the total dissolved solids in the sample.

APPENDIX C

Data and Results of Preliminary Economic Analysis

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APPENDIX C

DATA AND RESULTS OF PRELIMINARY ECONOMIC ANALYSIS

Analysis Procedure

The procedure used for these preliminary cost analyses on the production of ultrathin membrane reverse osmosis tubes was based on a modified* method of Zevnik and Buchanan.[1]

The Zevnik-Buchanan approach required the input of four types of information:

1. The *capacity* of the proposed process;
2. An assessment of the *process complexity;*
3. A process diagram for determining the number of *functional units;* and
4. A *construction cost index.*

From these, a total plant investment cost can be estimated. The above procedure was modified to give a cost per unit item of production based on operation 365 calendar days per year. These modifications included assessment of labor costs, raw material costs, utilities consumption, depreciation of capital equipment, and general overhead expenses.

In this method of cost analysis, the *capacity* of the proposed process is chosen, *e.g.,* ten million square feet of composite membrane tubular units per year.

The *process complexity* is related to the cost of capital equipment needed for the process. A "complexity factor" is derived from process parameters covering temperature, pressure, and need for corrosion-resistant metals and is calculated from Equation C-1 below:

$$CF = 2 \times 10^{(F_t + F_p + F_a)} \qquad (C-1)$$

where:

CF = complexity factor
F_t = temperature factor
F_p = pressure factor
F_a = alloy factor

*Private communication to North Star Research and Development Institute.

The maximum temperature to be anticipated in this process is 200°F (660° Rankine). From Zevnik and Buchanan, $F_t = 0.02$. This process will operate at atmospheric pressure. From Zevnik and Buchanan, $F_p = 0$.

The alloy factor would also be zero for this process because plastic-lined tanks would be used, and corrosion-resistant metals would not be required.

Then,

$$CF = 2 \times 10^{(F_t + F_p + F_a)}$$

$$= 2 \times 10^{0.02}$$

$$= 2.09$$

For each process a schematic diagram was drawn, and the number of *functional units* was determined. The investment cost per functional unit was determined from Figure C-1. The appropriate complexity factor was used at the given production capacity to determine the cost per functional unit in the process. Figure C-1 is based on a 1963 Nelson Refinery Construction Index (NRC) of 202. Construction costs since then have risen to the extent that the NRC Index now stands at 350.[2]

An assumption was used in applying Figure C-1 from the original Zevnik and Buchanan plot to membrane application. The production capacity of the original plot was in units of pounds per year. In the case of membrane-tube combination, the cost to produce one square foot was considered to be equivalent to one pound of commodity chemical. Although this assumption is admittedly inexact, it is considered sufficiently good for an order-of-magnitude estimate.

The process investment was calculated by multiplying the number of functional units by the cost per functional unit and by the NRC index ratio (based on 202). The process investment was further multiplied by a factor of 1.33 to make an allowance [1] for indirect investment costs for utilities and general facilities (land, building – "utilities and off-sites"). The resulting number then constituted the total investment.

By assuming a ten-year life for equipment, the investment cost was converted to an operating cost. To this was added other usual operating costs to obtain a total cost per unit of membrane area. The price for a 25-percent return on investment was then calculated.

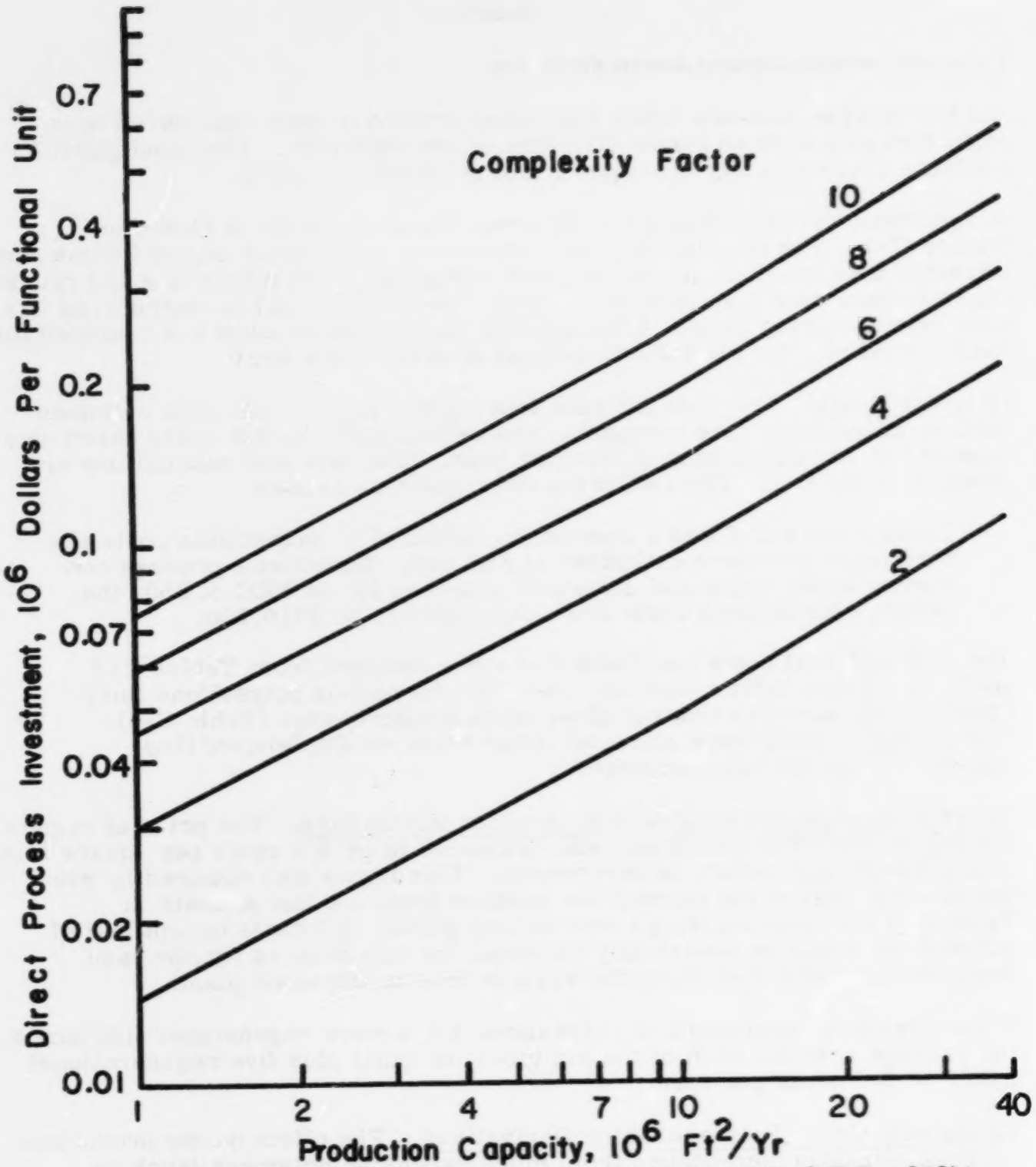

Figure C-1. Process Investment versus Capacity (NRC = 202)*

*From Zevnik and Buchanan[1].

Results

Tubes with Ultrathin Cellulose Acetate Membranes

All the reverse osmosis tubes discussed here have been considered to be eight feet long with an inside diameter of one-half inch. This configuration contains approximately one square foot of membrane area.

A schematic process diagram with seven functional units is shown in Figure C-2. The process includes fabricating polysulfone support films and ultrathin membranes. It also includes stripping of old membrane and recasting new membranes in used tubes. Both operations would be carried out in a tube manufacturing plant. Although only six functional units are required for each operation, the plant would consist of seven units total.

Original Tubes. The cost per tube (one square foot) of ultrathin cellulose acetate/polysulfone tube composite was estimated to be 9.5 cents based on a capacity of 10 million square feet per year. The data and calculations are given in Table C-1. The estimates were made as follows:

> Using Figure C-2 and a complexity factor of 2, investment costs per functional unit were estimated at $50,000. Based on a process containing seven functional units and adjusting for an NRC of 350, the process investment costs were calculated to be $810,000.

The raw material costs for Table C-1 were obtained from Tables C-2 and C-3. These tables show the costs for the porous polysulfone liner (Table C-2), and ultrathin cellulose acetate membranes (Table C-3). The chemical costs were obtained either from the *Oil, Paint, and Drug Reporter* [3] or the manufacturers.

Tubes with Regenerated Cellulose Acetate Membranes. The price of regenerating an ultrathin membrane was estimated to be 8.3 cents per square foot with a 25-percent return on investment. This figure was obtained by subtracting the cost of the polysulfone solution from the list of costs in Table C-1 and recalculating a new selling price. All costs except that of polysulfone would be essentially the same for this case as for the case presented in Table C-1 when the work is done in the same plant.

If the ultrathin membranes in polysulfone tubes were regenerated five times, the average cost for each of the six tubes (original plus five regenerations) would be 8.6 cents per tube.

Tubes with Other Polysaccharide Derivatives. The effect on the production costs of ultrathin membranes from more expensive polymers (such as cellulose methyl sulfonate O-propyl sulfonic acid) are considered here.

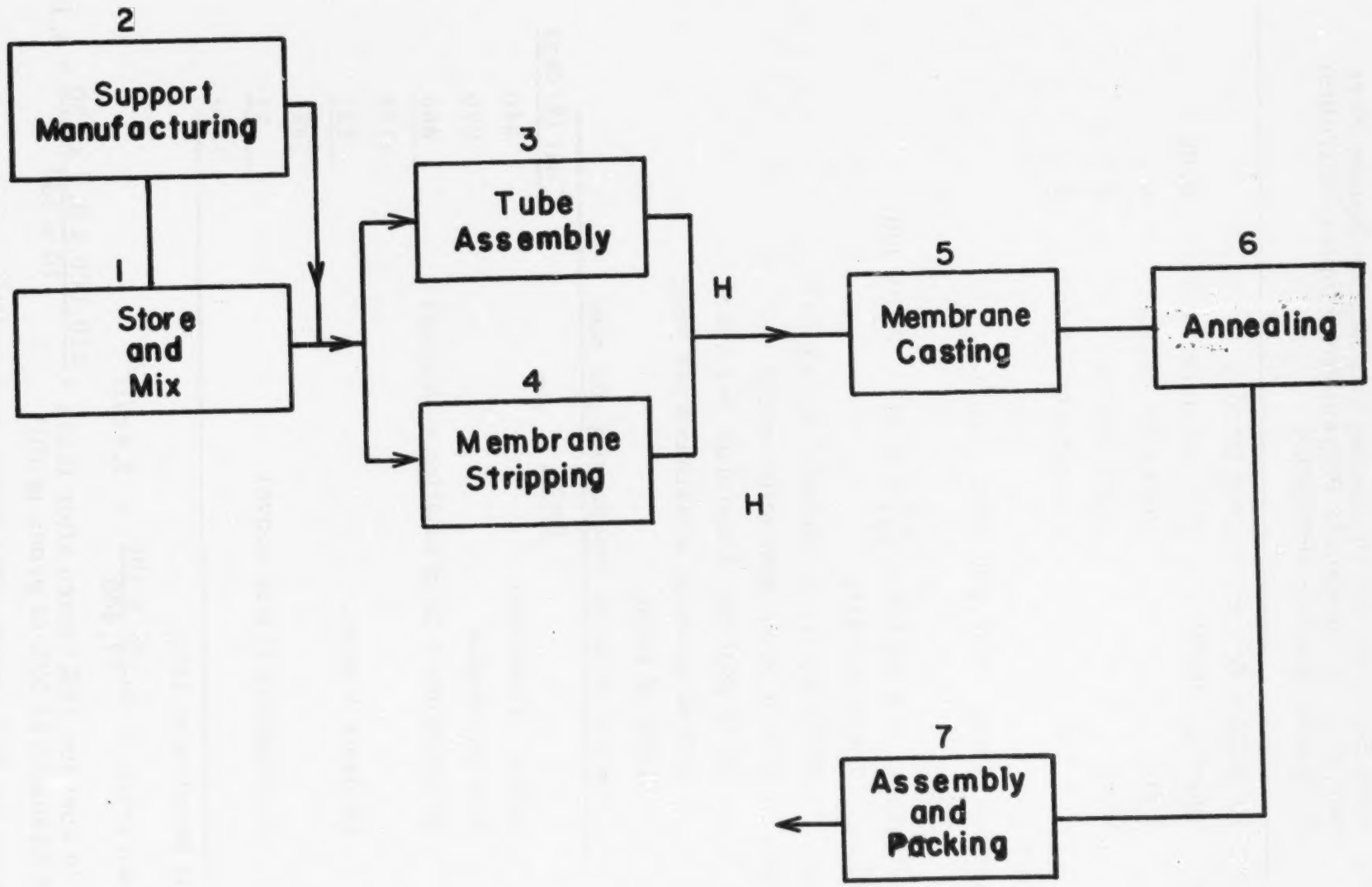

Figure C-2. Process Diagram Showing Functional Units of Reverse Osmosis Tube Manufacturing Plant

Table C-1. Cost Estimate for Producing Ten Million Square Feet per Year of Composite Polysulfone Support, Ultrathin Cellulose Acetate Membrane

Plant Size: 10 million ft^2/yr, 27,400 ft^2/day

Temperature: 200°F or 660°R — Temperature Factor: 0.02

Pressure: 1 atm — Pressure Factor: 0

Alloy: None — Alloy Factor: 0

Total Factor, F: 0.02 — Complexity Factor: 2

Functional Units: 7

Cost per Functional Unit: $50,000 (NRC = 202)

NRC Index: 350

Process Investment: $7 \times 50,000 \times \frac{350}{202} \times 1.33 = \$810,000$

Operating Labor: 7 men at $4/hr

Raw Materials: $270/day from Tables C-2 and C-3

Utilities + Misc: 20% of other production costs

Maintenance: 5% of process investment per year

Depreciation: 10% of process investment per year

Overhead: 100% of labor

Interest: 6% of process investment per year

Daily Costs:

Item	Cost ($/day)
Labor + Overhead	448
Raw Materials	270
Maintenance + Depreciation + Interest	466
	1184
Utilities + Misc.	237
	1421
Contingency (5% of above)	71
	1492

Price per Unit Membrane Area:

Break-even price $= \frac{1,492 \times 100}{27,400} = 5.4\,¢/ft^2$

Increase in cost for 25% return after taxes $= \frac{810,000 \times 0.5 \times 100}{10 \times 10^6} = 4.1\,¢/ft^2$
(Taxes assumed at 50% of gross profit)

Selling price for 25% return after taxes $= 9.5\,¢/ft^2$

Table C-2. Estimated Raw Material Costs of Polysulfone Tube Liners

Assume:

Film is cast from 15% by weight polysulfone and 85% dimethyl formamide solution

Cost of polysulfone is $1/lb

Cost of DMF is 24¢/lb

Film thickness is 2 mils

Specific gravity is 0.4

Then cost of materials is:

$$\frac{(0.15 \times 100 + 0.85 \times 24) \times 0.002 \times 62.4 \times 0.4}{0.15 \times 12} = 0.98¢/ft^2 \text{ or } \$268/day$$

Table C-3. Estimated Raw Material Costs for Ultrathin Cellulose Acetate Membrane

Assume:

Film is cast from 5% by weight CA and 95% ethyl acetate solution

Cost of CA is 70¢/lb

Cost of ethyl acetate is 13¢/lb

Membrane thickness is 1000 Å

Specific gravity is 1.3

Then cost of materials is:

$$\frac{(0.05 \times 70 + 0.95 \times 13) \times 1000 \times 10^{-8} \times 62.4 \times 1.3}{0.05 \times 2.54 \times 12} = 0.0084¢/ft^2 \text{ or } \$2.30/day$$

The raw material costs for these membranes are given in Tables C-4 and C-5. It is expected that the cost of the new polymer would be between $5 and $50 per pound.

From Tables C-4 and C-5, the total raw material cost for the tubes is virtually the same when they contain either cellulose acetate or other polysaccharide derivative membranes. The raw material cost comprises the only difference in the selling price of the tubes containing the two membranes. Thus, the selling price is unchanged for all practical purposes when polymers with an approximately 100-fold raw material cost increase are used. Due to their ultrathin nature, the extremely small amounts of the polymers that are necessary for the membranes in the tubes account for their insignificant effect on the total selling price of the tubes.

Effect of Plant Capacity on Tube Cost. The effect of reducing tube production to one million units per year is shown in Table C-6. The greatly increased cost of 40¢/ft^2 compared with 9.5¢/ft^2 for ten million units per year is due largely to the higher proportional cost of labor.

Table C-4. Estimated Raw Material Cost of Ultrathin Membrane of a Polysaccharide Derivative with a Cost of Five Dollars per Pound

Assume:

Film is cast from 5% by weight derivative and 95% ethyl acetate solution

Cost of derivative is $5/lb

Cost of ethyl acetate is 13¢/lb

Membrane thickness is 1000 Å

Specific gravity is 1.3

Then cost of materials is:

$$\frac{(0.05 \times 500 + 0.95 \times 13) \times 1000 \times 10^{-8} \times 62.4 \times 1.3}{0.05 \times 2.54 \times 12} = 0.020¢/ft^2$$

Table C-5. Estimated Raw Material Cost of an Ultrathin Membrane of a Polysaccharide Derivative with a Cost of Fifty Dollars per Pound

Assume:

Film is cast from 5% by weight derivative and 95% ethyl acetate solution

Cost of derivative is $50/lb

Cost of ethyl acetate is 13¢/lb

Membrane thickness is 1000 Å

Specific gravity is 1.3

Then cost of materials is:

$$\frac{(0.05 \times 5000 + 0.95 \times 13) \times 1000 \times 10^{-8} \times 62.4 \times 1.3}{0.05 \times 2.54 \times 12} = 0.14¢/ft^2$$

Table C-6. Cost Estimate for Producing One Million Square Feet per Year of Composite Polysulfone Support, Ultrathin Cellulose Acetate Membrane

Plant Size:	1.0 million ft^2/yr, 2,740 ft^2/day		
Temperature:	200°F or 660°R	Temperature Factor:	0.02
Pressure:	1 atm	Pressure Factor:	0
Alloy:	None	Alloy Factor:	0
Total Factor, F:	0.02	Complexity Factor:	2
Functional Units:	7		
Cost per Functional Unit:	$15,000 (NRC = 202)		
NRC Index:	350		
Process Investment:	$7 \times 15,000 \times \frac{350}{202} \times 1.33 = \$240,000$		
Operating Labor:	7 men at $4/hr		
Raw Materials:	$27/day		
Utilities + Misc:	20% of other production costs		
Maintenance:	5% of process investment per year		
Depreciation:	10% of process investment per year		
Overhead:	100% of labor		
Interest:	6% of process investment per year		

Daily Costs:

Item	Cost ($/day)
Labor + Overhead	448
Raw Materials	27
Maintenance + Depreciation + Interest	138
	613
Utilities + Misc.	122
	735
Contingency (5% of above)	37
Total	772

Price per Unit Membrane Area:

Break-even price $= \frac{772 \times 100}{2,740} = 28¢/ft^2$

Increase in cost for 25% return after taxes (Taxes assumed at 50% of gross profit) $= \frac{240,000 \times 0.5 \times 100}{1.0 \times 10^6} = 12¢/ft^2$

Selling price for 25% return after taxes $= 40¢/ft^2$

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2. *Oil and Gas Journal* (September 1970).

3. *Oil, Paint and Drug Reporter* (February 1970).

1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
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5 Organization

NORTH STAR RESEARCH AND DEVELOPMENT INSTITUTE
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Ultrathin Membranes*, Polysaccharide Derivatives*

27 Abstract

A series of new and ultrathin membranes with thicknesses from 250 to 5000 angstroms (1×10^{-6} to 2×10^{-5} inch) and consisting of various polysaccharide mixed esters and ethers were tested on microporous supporting films for improved reverse osmosis treatment of municipal wastewaters. From the screening studies with secondary effluents, ultrathin membranes prepared from two polymers (out of a total of 44) looked very promising: cellulose methyl sulfonate O-propyl sulfonic acid (CMSOPSA) and cellulose acetate O-propyl sulfonic acid (CAOPSA). The CMSOPSA membrane was found to be significantly less degradable by hydrolysis, and thus more stable than cellulose acetate.

Long-term (150 hours) testing of the CMSOPSA membrane with secondary effluent resulted in an average water flux of 34 to 36 gfd over the last 100 hours, and rejections of 96 percent for total dissolved solids, 94 percent for ammonia, and 83 percent for total organic carbon. The long-term flux decline (not due to fouling) was virtually zero over the last 100 hours of the test. A treatment with an enzyme-active laundry pre-soaking product was found to be effective in cleaning the membranes and restoring the flux to levels existing before fouling.

A preliminary economic analysis showed that, for a tubular configuration, a cost of approximately 10 cents could be expected for one square foot of the composite of membrane and microporous support film. This cost was insensitive to polymer raw material costs.

Abstractor L.T. Rozelle | Institution North Star Research and Development Institute

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